

A TEXT BOOK OF HEAT

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PREFACE

In the preparation of this book meant for engineering and science students, not only standard syllabus of Engineering degree classes and A.M.I.E. courses have been followed but also syllabi proposed by other Indian Universities have been consulted. The subject-matter both as regards the arrangement of chapter as well as contents of each chapter has been so set that the students may follow the courses easily. Keeping in view this background, the matter has been explained wherever required with diagrams. At the end of each chapter expected questions taken mostly from the various universities, A.M.I.E. and Engineering Colleges have been provided to make students know the type of questions set in the examination. The subject-matter has been dealt in M.K.S. systems and with the latest engineering developments in it. Sufficient numerical questions wherever necessary have been solved to explain applications of various formulae.

I am thankful to the Publishers, M/s. Dhanpat Rai & Sons, for undertaking the publication of this book.

AUTHOR

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CHAPTER I

EXPANSION OF SOLIDS

1.1. Expansion of solids. Solids, in general, expand on heating and the amount of expansion is proportional to the rise of temperature. The solid expands not only in its length but its surface area and volume also increase. The expansions of length, area and volume are respectively called **Linear expansion**, **superficial expansion** and **cubical expansion**.

1.2. Linear expansion. When a rod of a solid material is heated, it is found that its length increases, the increase in length is called **Linear expansion**.

Let L_0 be the length of a rod at 0°C . If the rod is heated to $t^\circ\text{C}$, its length becomes L_t , then

$$\text{Increase in length} = \Delta L = L_t - L_0$$

It is experimentally found that the increase in length ΔL is

- (i) directly proportional to the original length L_0
- (ii) directly proportional to the rise of temperature t and
- (iii) depends upon the nature of the material of the rod.

Combining all these factors we have

$$\begin{aligned} L_t - L_0 &= \alpha L_0 t \\ \text{or } L_t &= L_0 + \alpha L_0 t \\ &= L_0 (1 + \alpha t) \end{aligned} \quad \dots(i)$$

Where α is a constant depending upon the nature of the material and is called the **coefficient of linear expansion**.

From (i) we have

$$\alpha = \frac{L_t - L_0}{L_0 \times t} = \frac{\text{Increase in length}}{\text{original length} \times \text{rise in temp.}} = \frac{\Delta L}{L_0 t} \quad \dots(ii)$$

If L_0 = unit length and $t = 1^\circ\text{C}$, then

$$\alpha = \frac{\Delta L}{1 \times 1} = \text{Increase in length per unit length at } 0^\circ\text{C for } 1^\circ\text{C}$$

rise in temperature.

The coefficient of linear expansion of a solid is a very small quantity so it is not necessary that initial temperature may be 0°C . Hence the coefficient of linear expansion of a solid may in general be defined as *the increase in length per unit length per degree centigrade rise in temperature.*

If the length of solid is known at an initial temperature $t_1^\circ\text{C}$ (other than 0°C) its length at any other temperature $t_2^\circ\text{C}$ can be found out as follows.

Let L_1 = length of the rod at $t_1^\circ\text{C}$

L_2 = length of the rod at $t_2^\circ\text{C}$

From equation (ii) we have

$$L_1 = L_0 (1 + \alpha t_1)$$

and similarly

$$L_2 = L_0 (1 + \alpha t_2)$$

$$\text{or } \frac{L_2}{L_1} = \frac{1 + \alpha t_2}{1 + \alpha t_1}$$

$$= (1 + \alpha t_2) (1 + \alpha t_1)^{-1}$$

$$= (1 + \alpha t_2) (1 - \alpha t_1)$$

$= 1 + \alpha t_2 - \alpha t_1 +$ terms containing α^2 etc. which are very small and can be neglected.

$$= 1 + \alpha(t_2 - t_1)$$

$$\therefore L_2 = L_1 [1 + \alpha(t_2 - t_1)]$$

...(iii)

$$\text{and } \alpha = \frac{L_2 - L_1}{L_1(t_2 - t_1)}$$

...(iv)

From equation (iv) it is clear that the coefficient of linear expansion α is only a ratio and hence its unit is per $^\circ\text{C}$ or per $^\circ\text{F}$. Since a Fahrenheit degree is $5/9$ of a centigrade degree, coefficient of linear expansion per Fahrenheit degree is only $5/9$ of the coefficient of linear expansion per centigrade degree.

Table of coefficients of linear expansion

Substance	α per $^{\circ}\text{C}$
Aluminium	24×10^{-6}
Copper	16.5×10^{-6}
Brass	18.9×10^{-6}
Cast iron	11.1×10^{-6}
Stainless steel	10.4×10^{-6}
Mild steel	12.1×10^{-6}
Invar (alloy of nickel and steel containing 36% Ni)	0.9×10^{-6}
Nickel steel	13.0×10^{-6}
Silver	13.8×10^{-6}
Gold	14.0×10^{-6}
Tin	21.4×10^{-6}
Lead	27.6×10^{-6}
Platinum	8.9×10^{-6}
Tungsten	4×10^{-6}
Glass	9.5×10^{-6}
Glass pyrex	3.0×10^{-6}
Duralumin	22.6×10^{-6}

Example 1. A brass and an iron rod are each one metre long at 0°C . Find the difference in their lengths at 100°C . Coeff. of linear expansion of brass is 0.000019 and that of iron $= 0.000012$.

Length of each rod at 0°C $= 100$ cms.

Rise of temp. $t = 100^{\circ}\text{C}$

Length of brass rod at 100°C $= L_0(1 + \alpha t)$
 $= 100 (1 + 0.000019 \times 100)$
 $= 100.19$ cms.

Length of iron rod at 100°C $= 100 (1 + 0.000012 \times 100)$
 $= 100.12$ cms.

Difference between the lengths of the two rods at 100°C

$$= 100.19 - 100.12$$

$$= 0.07 \text{ cm.}$$

Example 2. A brass disc at 20°C has a diameter of 30 cm. and a hole cut in the centre is 10 cm. in diameter. Calculate the diameter of the hole when the temperature of the disc is raised to 50°C . The coeff. of linear expansion for brass $= 0.000018$.

Let the circumference of the hole at 20°C be L_1

$$\therefore L_1 = 2\pi r = 2\pi \times \frac{10}{2} = 10\pi \text{ cms.}$$

Suppose after heating, the radius of the hole becomes R , so that the circumference of the hole at 50°C is $L_t = 2\pi R$.

$$\text{Now } L_2 = L_1 [1 + \alpha (t_2 - t_1)]$$

$$\therefore 2\pi R = 10\pi [1 + 0.000018 \times (50 - 20)]$$

$$\text{or } 2R = 10.00540 \text{ cm.}$$

Hence diameter of the hole at $50^{\circ}\text{C} = 2R = 10.00540 \text{ cms.}$

Example 3. A metal rod of diameter one cm. measures 50 cms. in length at 20°C . When it is heated to 95°C . its length becomes 50.06 cms. What is the coeff. of linear expansion of the rod. What will be the length of the rod if it is cooled to 0°C .

$$\text{Length of the rod at } 20^{\circ}\text{C} = 50.0 \text{ cms.}$$

$$\text{Length of the rod at } 95^{\circ}\text{C} = 50.06 \text{ cms.}$$

$$\begin{aligned} \text{Increase in length} &= 50.06 - 50.0 \\ &= 0.06 \text{ cm.} \end{aligned}$$

$$\text{Rise in temperature} = 95 - 20 = 75^{\circ}\text{C}$$

$$\text{Coeff. of linear expansion } \alpha = \frac{\text{increase in length}}{\text{original length} \times \text{rise in temp.}}$$

$$= \frac{0.06}{50 \times 75} = 0.000016$$

Let L_0 be the length of the rod at 0°C , then

$$L_t = L_0(1 + \alpha t)$$

$$\begin{aligned} L_0 &= \frac{L_t}{1 + \alpha t} \\ &= \frac{50.0}{1 + 0.000016 \times 20} \\ &= 49.987 \text{ cms.} \end{aligned}$$

1.3. Practical Applications. The expansion of solids is utilised in several ways, in some cases it is a welcome effect while in others it is an adverse effect to be overcome. Some of the important applications where it serves a useful purpose are :—

(i) **Sealing wire in glass.** The expansion of platinum is very nearly equal to that of glass. Hence wires of platinum are used for sealing into glass. If we use any other material its expansion will be different from that of glass. Hence when glass cools after sealing of the wire, it will crack due to unequal expansion. Now a days special alloys of steel and nickle ($55\% + 45\%$) have been made of which the expansion is the same as that of glass. These are comparatively cheaper and have replaced platinum for this purpose.

(ii) **Prevention of bulging walls from collapsing.** The expansion and contraction of iron rods is utilised to prevent the bulging walls from collapsing. A few iron rods are passed through outwardly bulging walls across the building and are heated at the centre. The extremities of the rods are then tightly fixed by nuts and bolts to iron plates screwed to the wall, on the outside. When the rods cool and contract, the walls are pulled together and assume their proper positions.

(iii) **Riveting of boiler plates.** The boiler plates are rivetted with red hot rivets. These on cooling contract and grip the plates tightly. The joint is thus steam tight.

(iv) **Fitting of metal tyres on cart wheels.** To fix an iron tyre on a wooden wheel, the tyre is always made of a diameter a little less than that of the wheel. The tyre is heated and, as a result, it expands. It is then made to slide over the wheel. On cooling it contracts and grips the wheel very tightly.

(v) Sometimes, glass stoppers stick in the neck of the bottle too tightly to be opened by ordinary means. To remove the stopper the neck of the bottle is carefully heated. The neck expands but the stopper does not because very little heat is conducted to it. As a result the stopper becomes loose and can be easily opened.

(vi) The differential expansion of two solids is used in the construction of bimetallic strips used in thermostats and relays. These have been discussed in Art. 1.5.

Following are the examples where thermal expansion is a harmful effect to be overcome.

(i) When railway lines are laid some space is left between two rails to allow for expansion during summer. If this is not done the rails would expand and bend thereby causing derailment of trains. The arrangement showing how two rails are joined by fish plates bolted to them is shown in the Fig. 1.1. The holes through which the bolts joining the rails pass are oval in shape. This allows the

movement of the two rails in the direction of their lengths due to a change in temperature.

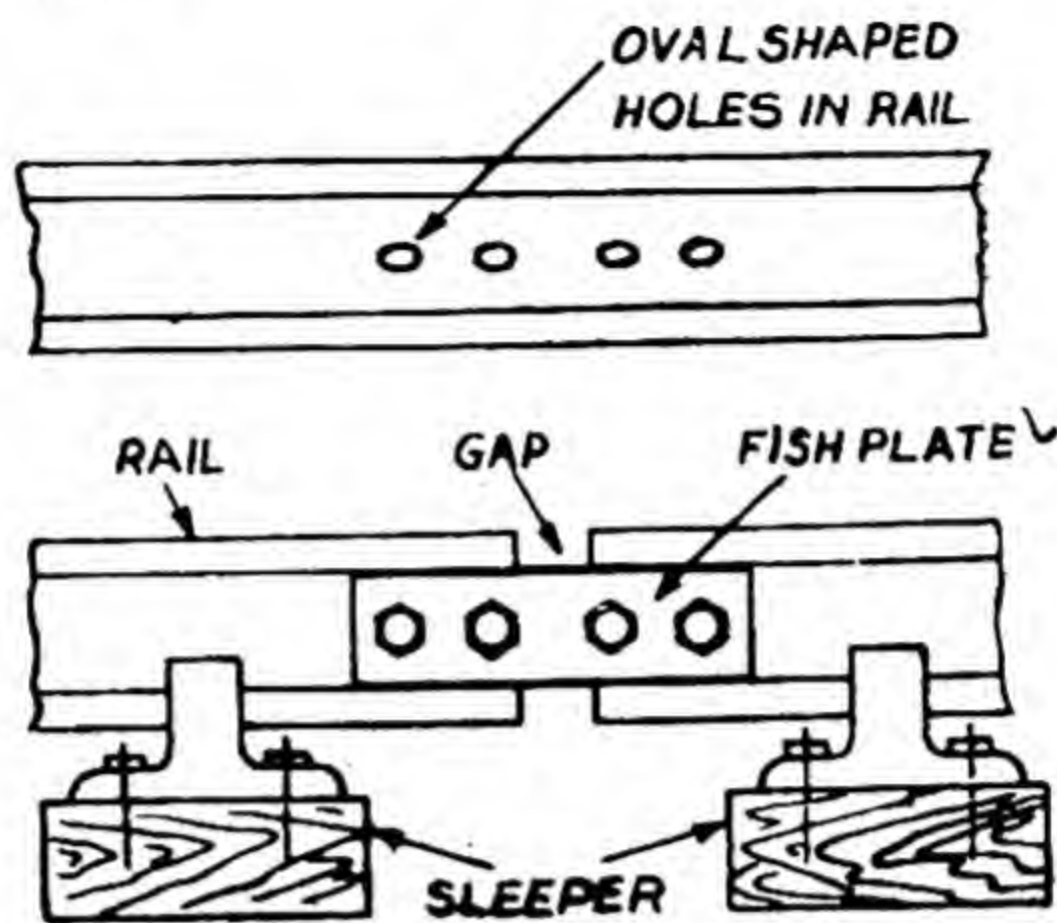


Fig. 1.1.

(ii) Similarly while constructing a railway bridge, provision must be made to accommodate the variation in length from winter to summer to prevent any damage to the bridge and its pieces. To achieve this the two ends of a long bridge are set on rollers so that the change in length may take place without damaging the structure.

(iii) Pipes carrying steam are given loops along their lengths to allow for change in length.

(iv) The telephone and electric wires between the poles always sag in hot weather and become stretched in cold weather. The wires, therefore, are so laid as to allow for this expansion and contraction.

(v) The reading of a scale is correct only at one temperature say $t_1^\circ\text{C}$. When the temperature of the scale is higher than $t_1^\circ\text{C}$ the distance between any two markings on it increases and its reading is therefore low. Similarly when the temperature is lower than $t_1^\circ\text{C}$ the reading becomes high.

If a scale measures a length L_1 correctly at $t_1^\circ\text{C}$, then at a temperature $t_2^\circ\text{C}$ the length measured as L_1 would have a true length.

$$L_2 = L_1 [1 + \alpha(t_2 - t_1)]$$

$$\therefore \text{true length} = \text{Observed length} [1 + \alpha(\text{rise of temp.})]$$

And correction to be applied to the observed length = observed length $\times \alpha \times$ rise in temperature

Now a days in practice no correction is applied because the tape used is made of **Invar**, which is an alloy of iron and nickle the expansion of which with rise in temperature is very small.

Example 4. A tape used for measuring distances is made of steel and is correct at a temperature of 15°C . If the tape is used for measuring

a distance of 700 metres when the temperature is 10°C . what will be the total error in the measured distance due to expansion of the steel tape? [α for steel $= 13 \times 10^{-6}$ per $^{\circ}\text{C}$.]

We know that

$$L_2 = L_1[1 + \alpha(t_2 - t_1)]$$

Where

L_2 = Actual length at 15°C and

L_1 = observed length at 10°C

$$\therefore 700 = L_1 [1 + 13 \times 10^{-6} (10 - 15)]$$

$$= \text{observed length} (1 - 65 \times 10^{-6})$$

$$\text{or observed length} = \frac{700}{(1 - 65 \times 10^{-6})} = 700(1 - 65 \times 10^{-6})^{-1}$$

$$= 700 (1 + 65 \times 10^{-6}) = 700 + 0.0455$$

$$= 700.0455$$

$$\text{Error} = +0.0455 \text{ metre}$$

(vi) Concrete roads and floors are never laid in one piece. These are laid in sections and expansion channels are provided between the sections. Without these expansion channels, the concrete would soon be broken up due to the large forces caused by the expansion.

(vii) A thick glass tumbler usually cracks if very hot liquid is poured into it. The reason is that inside of the tumbler gets heated and expands even before the outside layer just becomes warm. Thus unequal expansion of the glass produces strain in the glass and this causes the tumbler to break. In a thin-walled beaker, however there is uniform heating and uniform expansion everywhere.

The expansion of pyrex glass is about $\frac{1}{3}$ rd that of expansion of ordinary glass. It is for this reason that the pyrex glass can be heated without cracking.

(viii) The moving parts of machinery such as axles and shafts, are gaured against their expansion due to the heat produced by the use of lubricating oils.

(ix) A pendulum is used in a clock to keep time. We know that the time period (time of oscillation) of a simple pendulum is given by

$$t = 2\pi \sqrt{\frac{l}{g}} \text{ where } l \text{ is the length of the pendulum and } g \text{ the}$$

acceleration due to gravity. The pendulum used in a clock is not a simple pendulum but is a compound pendulum consisting of a metal bob suspended by a thin metal rod. Hence if the length of the pendulum is increased due to rise in temperature, the time of oscillation increases and clock loses. If the length decreases due to fall in temperature, the pendulum swings faster, the time of oscillation becomes less and the clock gains. Thus a clock will lose time in summer and gain in winter, unless the pendulum is compensated against the effect of expansion.

There are several methods of compensating the pendulum for

change in temperature. Probably the best known is **Harrison's grid-iron pendulum**. The principle of this pendulum is explained below.

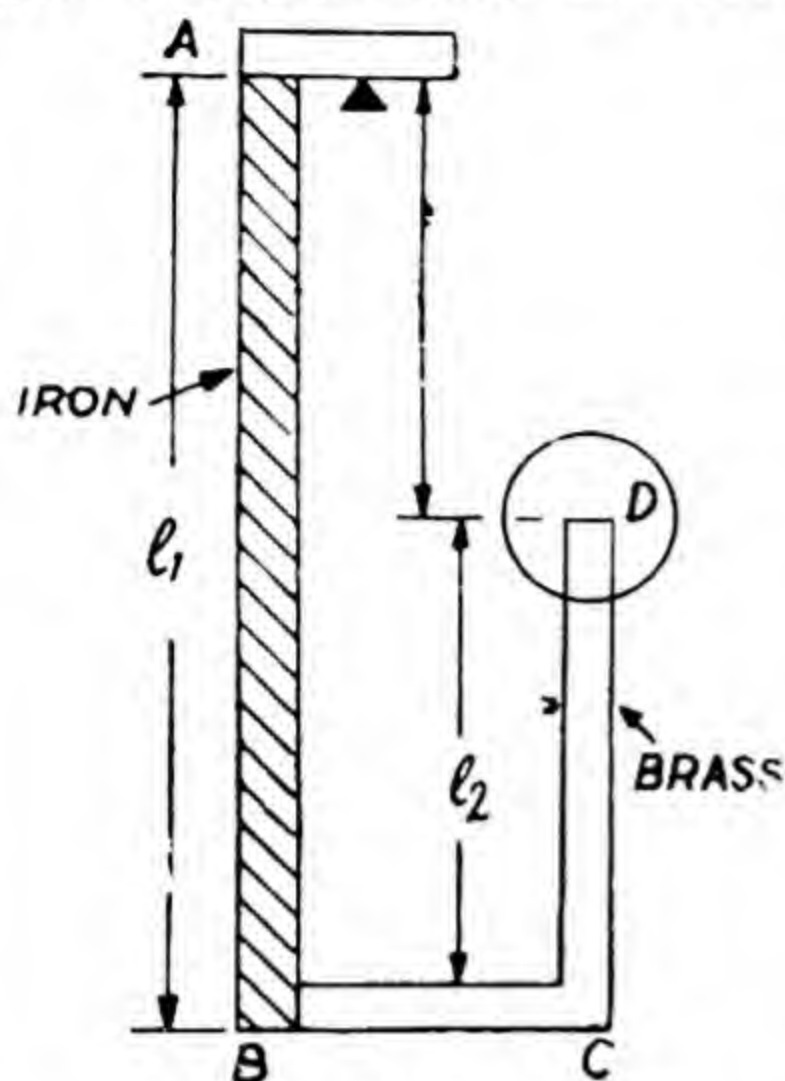


Fig. 1.2.

If l_1 is the length of iron rod AB and l_2 that of the brass rod CD and α_1 and α_2 their coefficients of linear expansion respectively then in order that their expansion may be the same for any rise of temperature.

$$l_1 \alpha_1 t = l_2 \alpha_2 t$$

or

$$l_1 \alpha_1 = l_2 \alpha_2$$

\therefore

$$\frac{l_1}{l_2} = \frac{\alpha_2}{\alpha_1}$$

Hence, for compensation, the lengths of the two rods should be in the inverse ratio of their coefficients of linear expansion.

Harrison's grid iron pendulum is constructed on this principle. It consists of a number of brass rods (shown by double lines) and steel rods (shown by thick lines) arranged alternately on a common frame suspended from the point A . There are 9 parallel rods out of which 4 are made of brass and 5 of steel. The bob is carried by the central steel rod. The ends of the rods are attached to cross bars in such a way that the steel rods expand downwards and tend to lower the position of the bob B while the brass rods expand in the upward direction and tend to raise the bob B . In order that the pendulum may keep correct time the distance bet-

Let two parallel rods AB and CD made of two different materials, iron and brass of different lengths be joined by a cross bar BC . The system is suspended at A and the end D carries a bob which is free to vibrate. With the rise in temperature, the rod AB will expand in the downward direction while the rod CD will expand in the upward direction. If the lengths of the rods are such that the downward expansion of AB is equal to the upward expansion of CD , the centre of gravity of the bob will remain in the same position and, therefore, the effective length AD of the pendulum will remain unchanged.

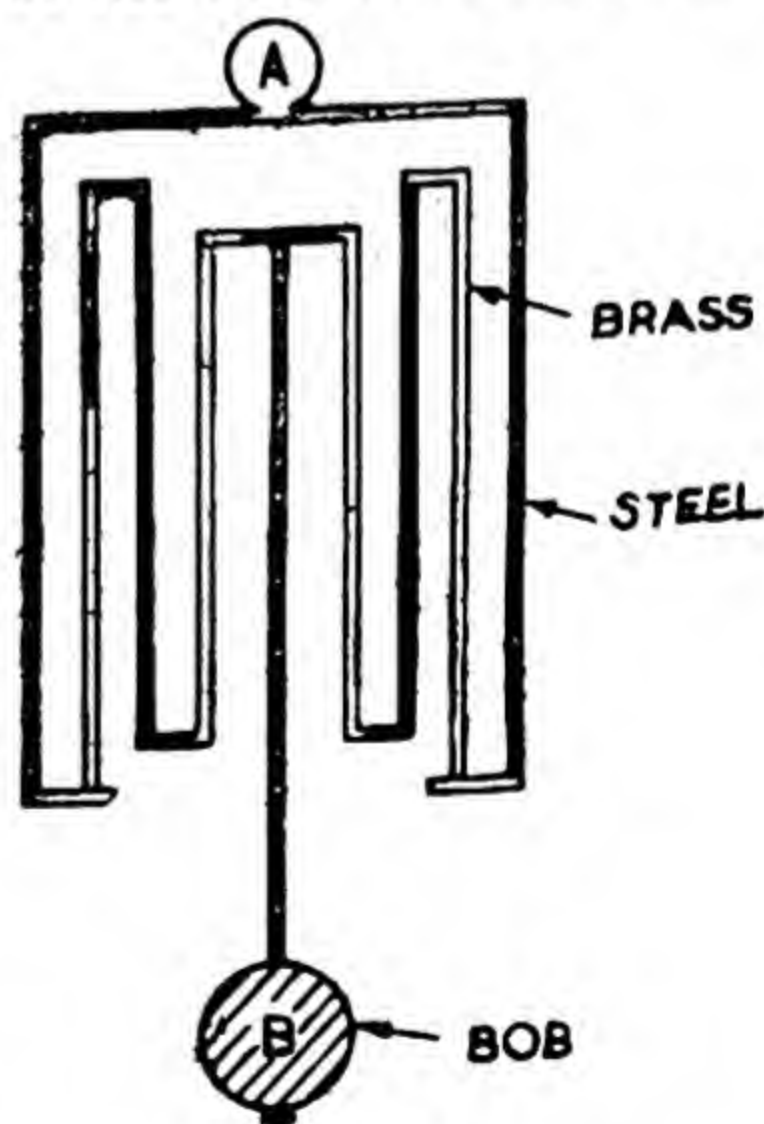


Fig. 1.3.

the distance bet-

ween the point of suspension and centre of gravity of the pendulum should remain the same at all temperatures.

As is clear from Fig. 1.3 all the rods except the central rod are in pairs. If there are 5 steel rods and 4 brass rods, the effect of five steel rods is the same as that of three and the effect of four brass rods is the same as that of two. The pendulum is so designed that the length of the three steel rods is $\frac{19}{12}$ times the length of the two brass rods. Since the coefficient of expansion of brass (0.000019) is $\frac{19}{12}$ times that of steel (0.000012), their expansions are equal and opposite and the centre of gravity of the bob remains in the same position.

A compensated pendulum used in clocks to keep correct time cannot be used in a watch or a time piece. In these an arrangement known as **Balance Wheel** is used. It essentially consists of two or three curved segments as shown in the Fig. 1.4. The wheel is supported

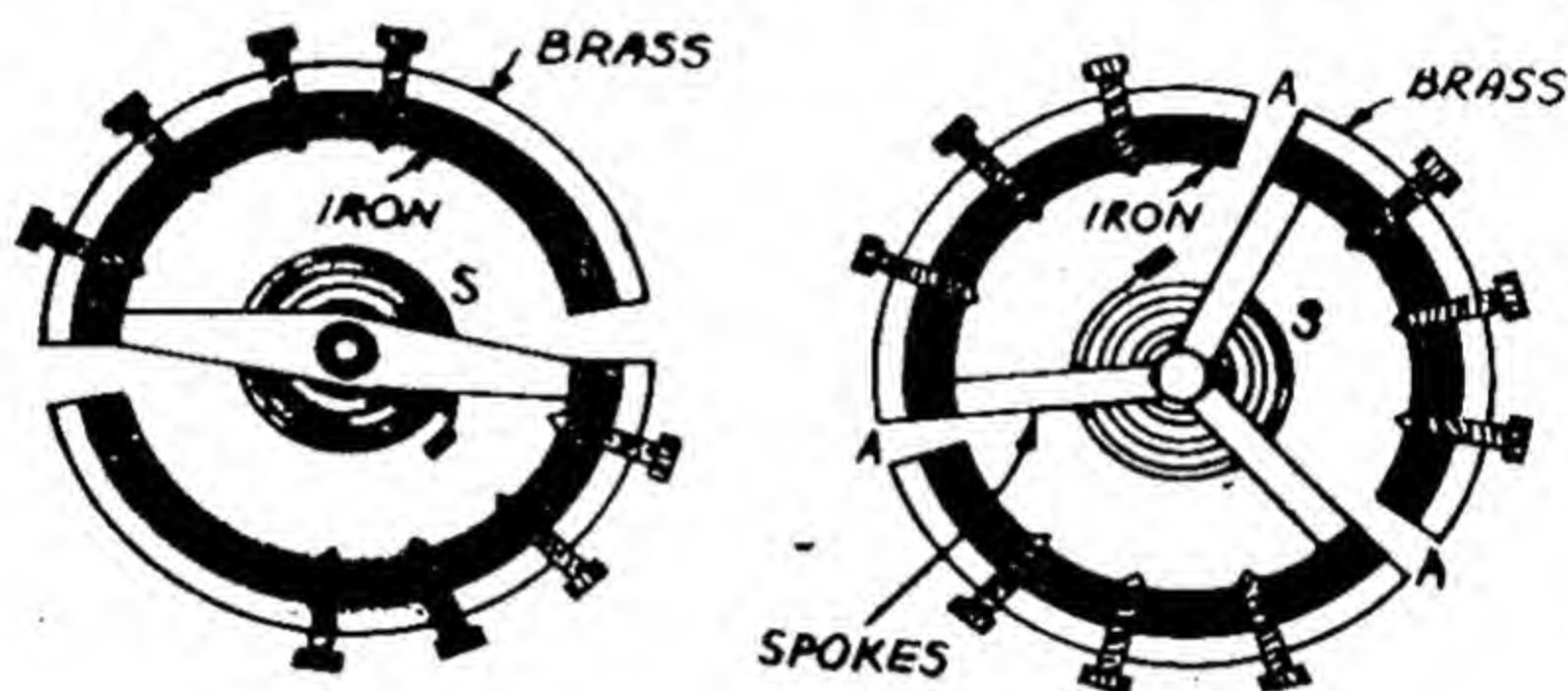


Fig. 1.4

on a vertical axis and oscillates under the influence of the hair spring S . The time period of the balance wheel is given by

$$t = 2\pi \sqrt{\frac{I}{C}}$$

(i) Where I is the moment of inertia of the balance wheel which in turn depends upon the radius of the wheel.

(ii) and C is a constant depending upon the elastic properties of the spring. It is the couple required to produce a unit angular twist in the hair spring.

When temperature rises, I increases, due to the expansion of the radial arms of the wheel, and C decreases due to the weakening of the elasticity of the spring. Both these factors increase the time of oscillation of the wheel and hence make the watch to run slow.

This trouble is overcome by making the rim of the balance wheel out of a bimetallic strip of brass and iron. The material of

higher coefficient of linear expansion like Brass is used on the outside and iron which has smaller coefficient of linear expansion is used on the inner side. The rim is made in two or three segments, each part being supported by a *spoke* of the wheel. Each segment of the wheel also carries small screw weights.

When the temperature rises, the increase in the length of the spoke causes the points *A* to recede from the centre of the wheel and the elasticity of the hair spring also becomes less. As a result the balance wheel tends to move slower. But at the same time, the free ends of the segments of the wheel curve inward, thereby decreasing the effective radius of the wheel and hence the wheel tends to move faster. These two tendencies, one making the wheel to move slower and the other making it to move faster, are made to compensate each other so that the time period remains the same at all temperatures. Exact compensation is obtained by adjusting carefully the screw weights on the three segments of the wheel the screws near the free ends tend to increase the compensation while those near the fixed ends produce an opposite effect. Only precision watches such as chronometers and wristlets are provided with compensated balance wheels.

With the introduction of **Invar** steel in the manufacture of pendulums and balance wheels the problem of compensation has been eliminated to a great extent, on account of the exceptionally small coefficient of expansion of this alloy. Since however, invar has a rather high magnetic susceptibility and is affected by changes in earth's magnetic fields, other alloys such as **Elinvar**, (steel nikel alloy) of smaller suceptibility and of negligible value of coefficient of expansion havebeen produced and utilized. In modern watches balance wheel is made of *invar* having a hair spring made of *elinvar* (steel-nickle alloy).

1.4. Influence of temperature on the time period of clocks.

The time of oscillation of a clock pendulum is given by

$$T = 2\pi \sqrt{\frac{l}{g}}$$

Where l = length of the pendulum.

g = acceleration due to gravity.

When temperature changes, the length of the pendulum of a clock changes and hence the time period is also affected.

At temperature t_1 , the time period

$$T_1 = 2\pi \sqrt{\frac{l_1}{g}}$$

...(i)

At temperature t_2 , the time period

$$T_2 = 2\pi \sqrt{\frac{l_2}{g}} \quad \dots(ii)$$

Dividing (ii) by (i) we have

$$\frac{T_2}{T_1} = \sqrt{\frac{l_2}{l_1}} \quad \dots(iii)$$

Now $l_2 = l_1 [1 + \alpha (t_2 - t_1)]$

$$\therefore \frac{l_2}{l_1} = 1 + \alpha (t_2 - t_1)$$

Substituting in equation (iii) we have,

$$\begin{aligned} \frac{T_2}{T_1} &= [1 + \alpha(t_2 - t_1)]^{\frac{1}{2}} \\ &= [1 + \frac{1}{2} \alpha(t_2 - t_1)] \text{ neglecting squares and higher powers of } \alpha(t_2 - t_1) \end{aligned}$$

$$\text{or } \frac{T_2}{T_1} - 1 = \frac{1}{2} \alpha(t_2 - t_1)$$

$$\text{or } \frac{T_2 - T_1}{T_1} = \frac{1}{2} \alpha(t_2 - t_1)$$

$$\text{or } \frac{dT}{T} = \frac{1}{2} \alpha (t_2 - t_1) \quad \dots(iv)$$

$\frac{dT}{T}$ = Fractional change of period with the change in temperature.

Hence loss or gain per day = $dT \times 3600 \times 24$ seconds.

If the value dT/T is positive the clock will lose time and if it is negative it will gain time.

Example 5. The pendulum of a clock is made of brass whose coefficient of linear expansion is 1.9×10^{-5} per degree. If the clock keeps correct time at 20°C , how many seconds per day will it lose at 35°C . Prove any formula used. (A.M.I.E.)

Fractional change in time period when temperature changes from 20°C to 35°C .

$$\begin{aligned} \frac{dT}{T} &= \frac{1}{2} \alpha(t_2 - t_1) \\ &= \frac{1}{2} \times 1.9 \times 10^{-5} (35 - 20) \\ &= \frac{1}{2} \times 1.9 \times 10^{-5} \times 15 \\ &= 14.25 \times 10^{-5} \end{aligned}$$

This means that the clock loses 14.25×10^{-5} seconds for each second interval. Hence the **loss** per one day would be

$$\begin{aligned} &= 14.25 \times 10^{-5} \times 3600 \times 24. \\ &= 12.3 \text{ Seconds} \end{aligned}$$

Example 6. A clock which keeps correct time at 20°C has a pendulum made of brass. How many seconds will it gain per day when the temperature falls to freezing point? α for brass $= 0.000019$ per $^\circ\text{C}$.

Fractional change in time period when temperature changes from 20°C to 0°C .

$$\frac{dT}{T} = \frac{1}{2} \alpha (t_2 - t_1)$$

As $t_2 - t_1$ is negative the clock will gain time :

Gain in time per second.

$$\begin{aligned} &= \frac{1}{2} \alpha (t_2 - t_1) \\ &= \frac{1}{2} \times 1.9 \times 10^{-5} (0 - 20) \\ &= -19 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} \text{Gain in time per day} &= 3600 \times 24 \times (-19 \times 10^{-5}) \\ &= -16.416 \text{ sec.} \end{aligned}$$

Example 7. Find the change in the period of oscillation of a pendulum of thin brass wire when the temperature changes from 20°C to 25°C . if the pendulum is 122.0 cm. long at the former temperature. Coefficient of linear expansion of brass is 1.9×10^{-5} per $^\circ\text{C}$. Given that $g = 980 \text{ cms./cm}^2$.

Fractional change in time period is given by

$$\begin{aligned} \frac{dT}{T} &= \frac{1}{2} \alpha (t_2 - t_1) \\ &= \frac{1}{2} \times 1.9 \times 10^{-5} (25 - 20) = 4.75 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} \text{Now } T &= 2\pi \sqrt{\frac{l}{g}} = 2\pi \sqrt{\frac{122}{980}} \\ &= \frac{2\pi}{\sqrt{10}} \times 1.12 = 2.23 \text{ sec.} \end{aligned}$$

\therefore Change in time period

$$dT = 4.75 \times 10^{-5} \times 2.23 = 10.6 \times 10^{-5} \text{ sec.}$$

Example 8. An iron clock pendulum makes 86407 oscillations in one day. At the end of the next day the clock has lost 12 seconds. Find the change in the temperature. Coeff. of Linear expansion for iron $= 1.17 \times 10^{-5}$ per $^\circ\text{C}$.

The number of seconds in a day = 86400 seconds.

On the first day the clock pendulum makes 86407 oscillations

$$\text{Period of one oscillation } T_1 = \frac{86400}{86407} \text{ sec.}$$

On the next day the clock pendulum makes $86407 - 12 = 86395$ oscillations

$$\text{Period of one oscillation } T_2 = \frac{86400}{86395} \text{ sec.}$$

$$\text{Now for a pendulum. } T_1 = 2\pi \sqrt{\frac{l_1}{g}}$$

where l_1 = length of the pendulum on the first day at $t_1^\circ\text{C}$ and

$$T_2 = 2\pi \sqrt{\frac{l_2}{g}} \text{ where } l_2 = \text{length of the pendulum on the next day at } t_2^\circ\text{C.}$$

$$\therefore \frac{T_2}{T_1} = \sqrt{\frac{l_2}{l_1}}$$

$$= \sqrt{1 + \alpha(t_2 - t_1)} = [1 + \alpha(t_2 - t_1)]^{\frac{1}{2}}$$

$$\text{or } \frac{86407}{86395} = \left[1 + \frac{1}{2} \alpha (t_2 - t_1) \right]$$

$$\text{or } \frac{86407}{86395} = 1 + \frac{1}{2} \times 1.17 \times 10^{-5} \times (t_2 - t_1)$$

$$\therefore \text{Change in temperature } t_2 - t_1 = \frac{\frac{86407}{86395} - 1}{\frac{1}{2} \times 1.17 \times 10^{-5}} = \frac{12 \times 2 \times 10^5}{86395 \times 1.17} = 23.8^\circ\text{C}$$

Example 9. A brass pendulum keeps correct time at 12°C . If it loses 6 seconds in a day when temperature is 19.5°C , calculate the coefficient of linear expansion.

$$\begin{aligned} \text{The fractional change in time period } \frac{dT}{T} &= \frac{1}{2} \alpha (t_2 - t_1) \quad \dots (1) \\ &= \frac{1}{2} \alpha (19.5 - 12) = \frac{1}{2} \alpha 7.5 \end{aligned}$$

$$\text{Now Loss per day} = dT \times 86400 = 6$$

$$\therefore dT = \frac{6}{86400}$$

As the clock keeps correct time at 12°C

$$\therefore T = 1 \text{ sec.}$$

$$\text{and } \frac{dT}{T} = \frac{1}{2} \alpha 7.5$$

$$\text{or } \frac{6}{86400} = \frac{1}{2} \alpha 7.5$$

$$\text{Hence } \alpha = \frac{6 \times 2}{86400 \times 7.5} = 18.5 \times 10^{-6} / ^\circ\text{C}$$

1.5. Differential expansion. From the table of coefficients of linear expansion, we find that the coefficient of linear expansion of brass is nearly $\frac{3}{2}$ times that of iron so that a brass strip will expand $\frac{3}{2}$ times as much as iron when heated through the same range of temperature.

Consider a strip of brass and iron rivetted together so as to form a composite bar. If this bar is heated, it will be found to bend because of the unequal expansion of the metals. Expansion of brass being greater than that of iron, brass will lie on the outer side of curve when hot. Similarly when cooled the brass will lie on the inner side, its contraction being greater than that of iron. Such a compound or composite bar is known as a **bimetallic strip**.

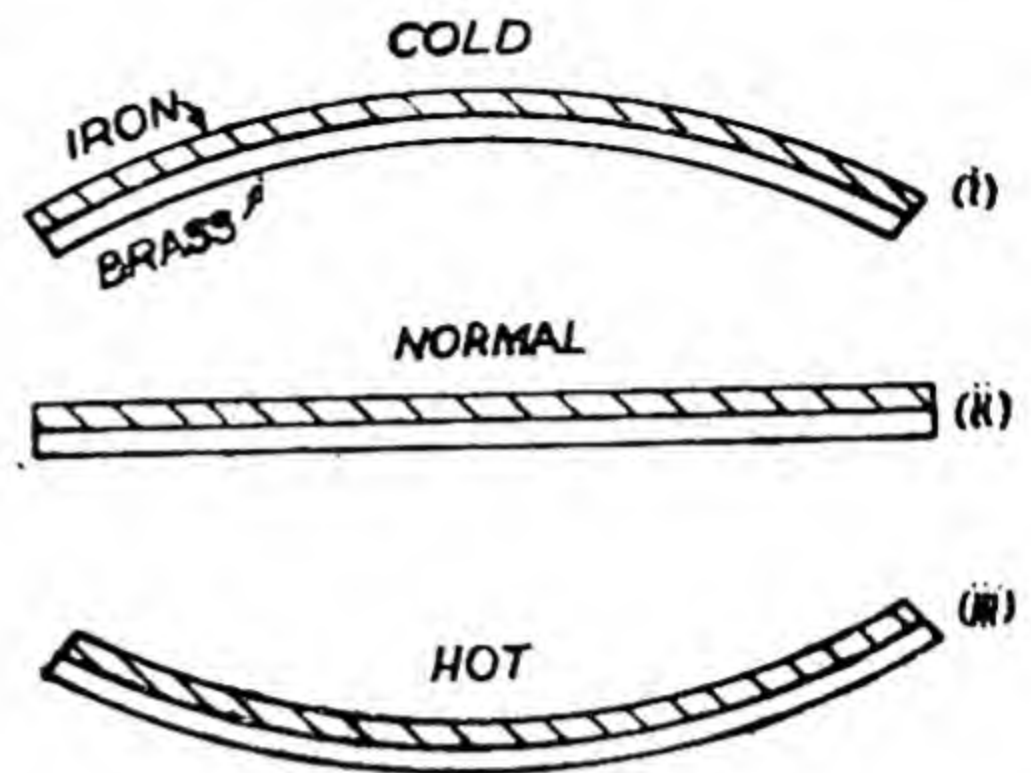


Fig. 1.5

Bimetallic strips are used in metal thermometers, in balance wheels used in watches and in thermostats for regulating the temperature and also for controlling many electric devices by temperature changes.

1.6. Thermostat. A thermostat is a device containing a bime-

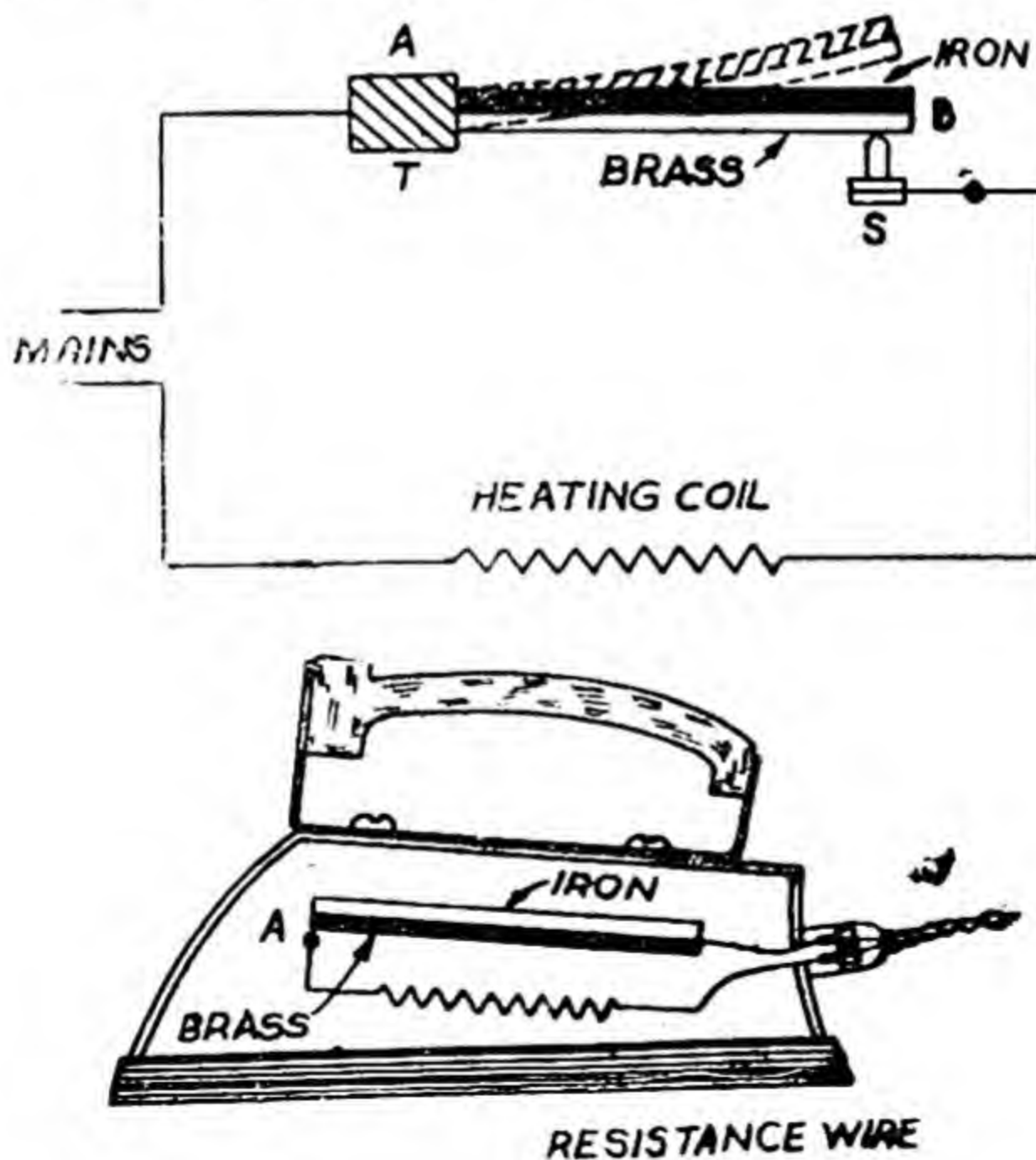


Fig. 1.6

tallic strip which is used for maintaining any temperature constant

at a given value. The expansion or contraction of the bimetallic strip can be made to make or break two electrical contacts at the desired temperature. The thermostat can be used to control the temperature in a refrigerator, or an electric iron or a room heater. Let us see how it helps to control the temperature in an electric iron.

The thermostat consists of a bimetallic strip of brass and iron fixed at the end *A* and free to move at the end *B* which is in contact with the screw *S*. When the arrangement is connected to the supply mains through the heating coil *H*, the current flows. As soon as the heat developed in the heating coil reaches the desired maximum value, the bimetallic strip also gets heated and curves upward due to the unequal expansion of brass and iron. This breaks the circuit and stops the flow of current. On cooling, the bar straightens again, and the contact is restored which completes the circuit. The temperature is thus maintained constant.

The use of a bimetallic strip in automatic **Fire Alarms** is shown in the Fig. 1.7. The action of the fire alarm is based upon the bending of a bimetallic strip on heating. Such type of thermostats are placed at many points in a big building where there is a danger of fire. The end *B* is connected through a bell and a battery to the screw *S* which is not in contact with the end *A*. If fire breaks out or temperature at a given point in a building rises beyond a certain point, the bimetallic strip gets heated and bends. This makes the contact of the screw *S* and thereby the bell circuit is completed. An alarm is thus raised by ringing of the bell.

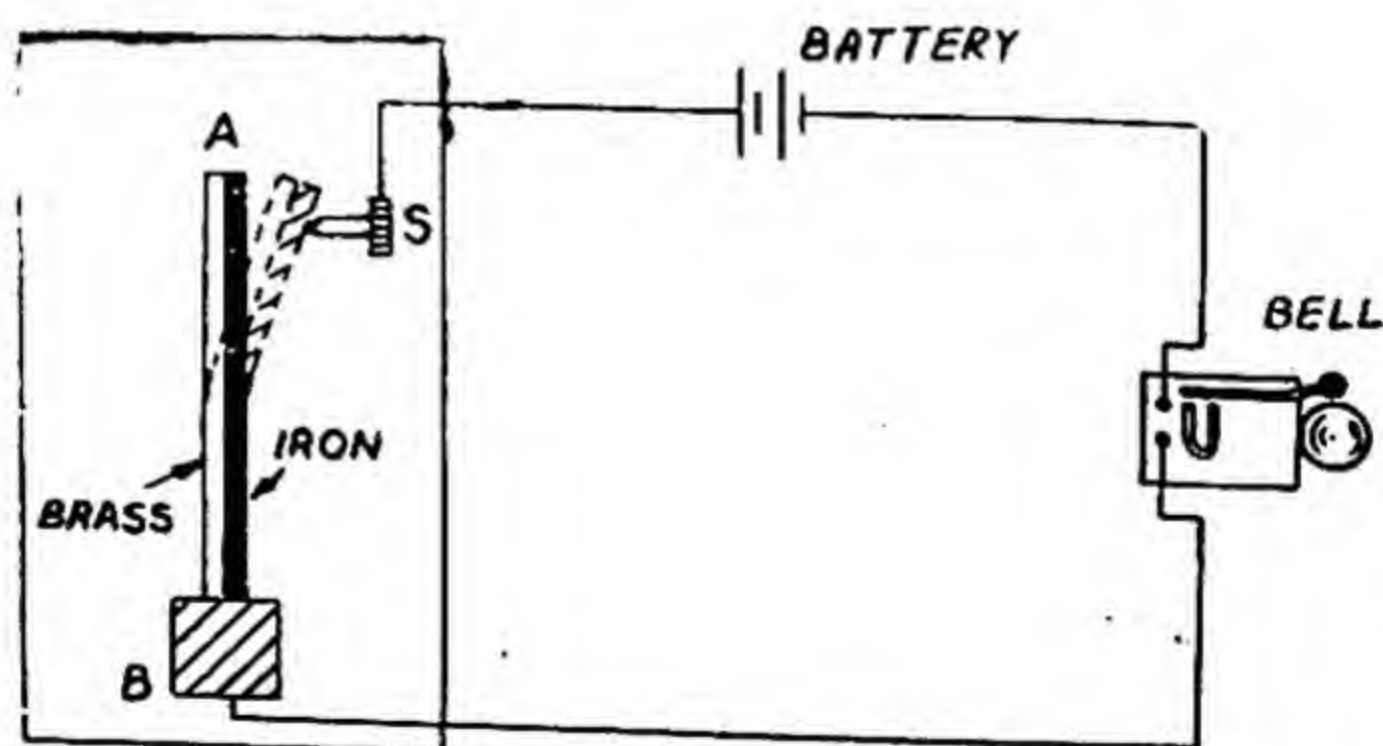
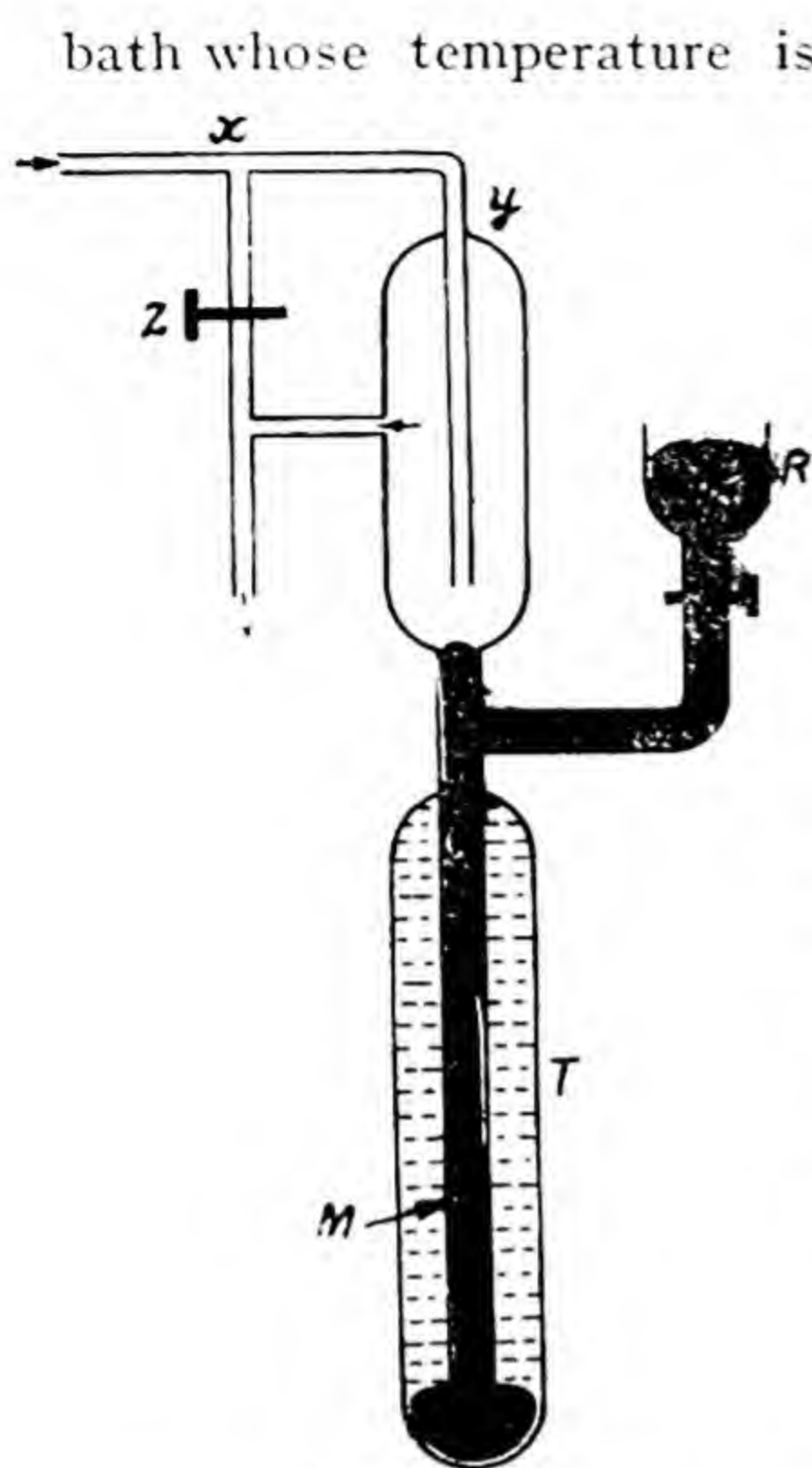


Fig. 1.7.

1.7. (a) Toluene Liquid Thermostat. If a glass bulb containing toluene, benzene, alcohol, or some such substance possessing a large coefficient of expansion, is placed in a bath of water or oil, it can be used as a **thermostat**. Toluene thermostat consists of a long tube *T* which is filled with a liquid such as toluene. The liquid is in contact with a mercury tube *M*. The bulb *T* is immersed in the



bath whose temperature is to be maintained constant. The bath is heated by a burner and the gas supply for it enters through the tube x , flows through the tube y as shown by arrows. As the temperature rises, the expansion of the toluene in the bulb T forces the mercury up the tube M until it closes the opening of y and stops the supply of gas reaching the heater. Actually a small side tube Z allows some little gas to pass in order to keep the flame burning, but the heat supplied is not sufficient to maintain the temperature of T . Hence, the toluene contracts, the opening of y is increased and more gas passes to the burner to heat the bath. By regulating the amount of mercury in the reservoir R the temperature of the bath can be kept constant at any desired value, accurate to one or two degrees.

Fig. 1.8
In the case of electric heater, the tubes at x and y are removed, and their places are taken by two platinum wires. One wire is sealed into M at any convenient position and the second one takes the place of the tube x . The use of a condenser in parallel with the contacts prevents sparking when the circuit is broken and the heating current cut off and thus avoids contamination of the mercury surfaces.

It is of importance to ensure that the bath is kept well stirred. With properly constructed thermostats the temperature of the bath can be kept constant accurate to 0.01°C . Such a thermostat can be used up to a temperature of about 100°C .

1.7. (b) **Vapour operated thermostat.** The principle of operation of

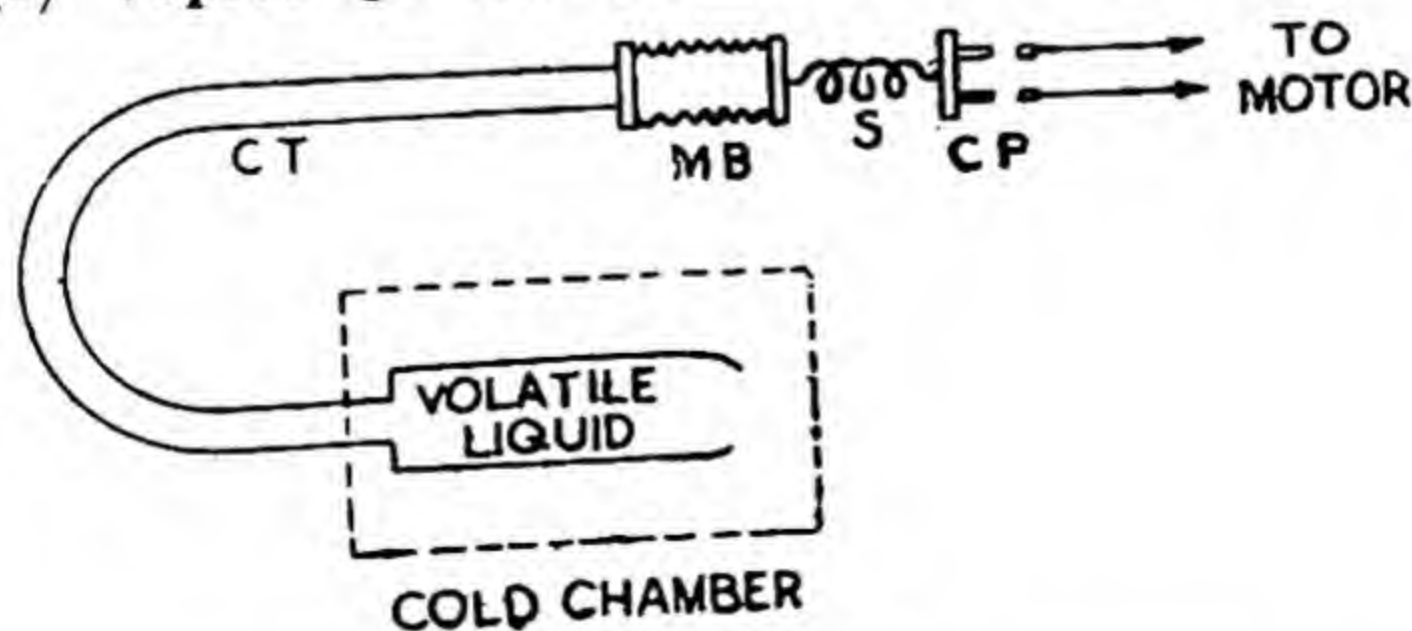


Fig. 1.9

such a thermostat is often used in refrigerators as shown in Fig. 1.9.

In this form of thermostat a volatile liquid is filled in a bulb which is placed in the cold chamber of the refrigerator whose temperature is required to be controlled. The change of temperature causes the change of vapour pressure in the bulb which in turn causes expansion and contraction of metallic bellows (MB) which further makes and breaks the contacts of the electric motor of refrigerator. Now, when the temperature of the chamber rises, the increase in vapour pressure is communicated as shown in the capillary tube into the metallic bellows, makes the electric contacts and thus starts the refrigerator motor.

When the temperature falls below the required value, the metallic bellows contract due to decrease in vapour pressure which breaks the contacts and stops the motor.

1.8. Laboratory method of determining the co-efficient of linear expansion. A simple method commonly used in the laboratory to determine the co-efficient of linear expansion makes use of the apparatus shown in fig. 1.10.

The apparatus consists of a rod CD of a given material about 60 cms. long enclosed in a wide tube supported on two supports fixed on the base of the apparatus. The ends of the outer tube are closed by means of corks through which pass the ends of the rod CD . One end of the rod is made pointed and the other is kept flat.

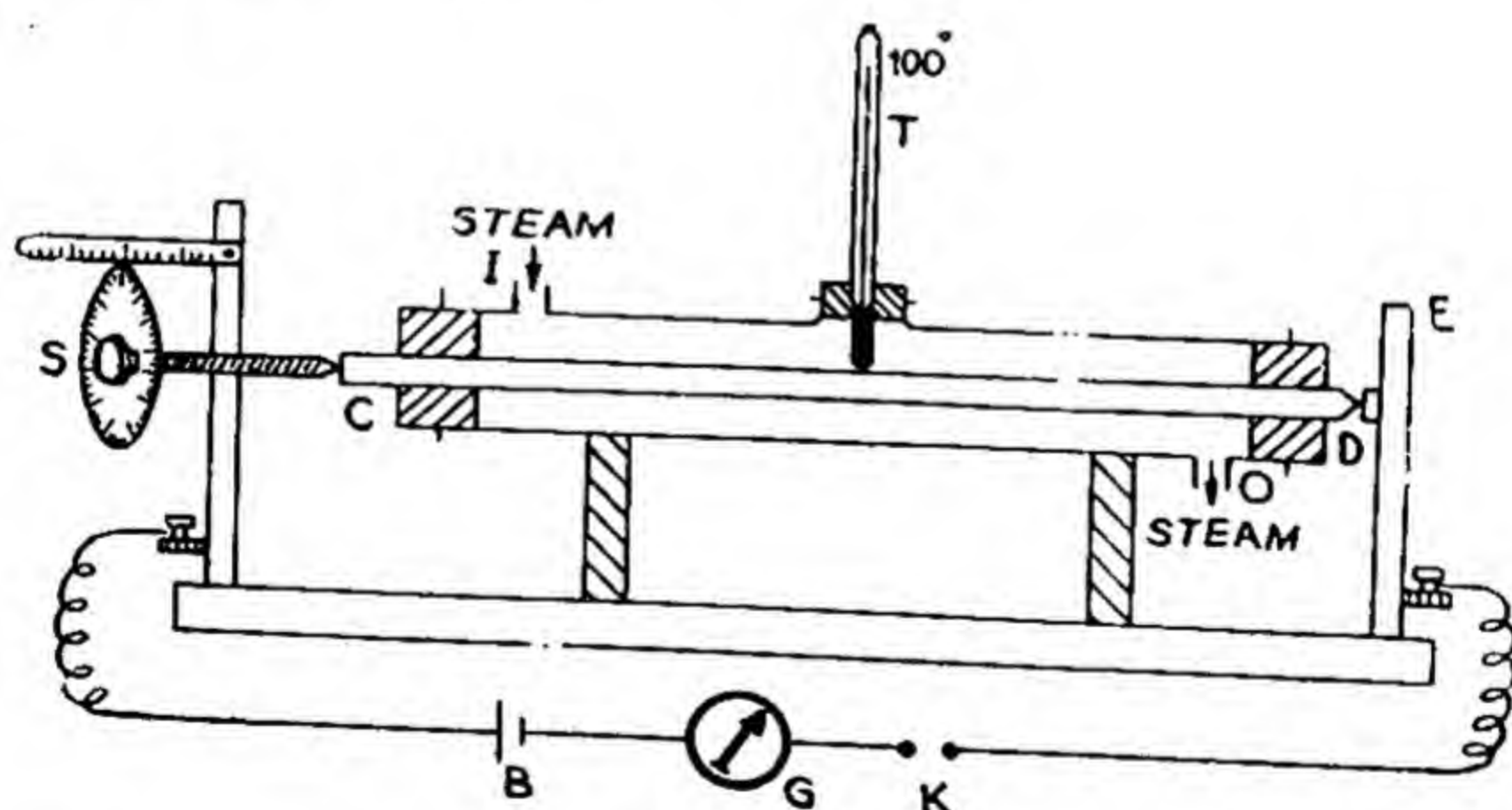


Fig. 1.10

The outer jacket is provided with two small side tubes I and O , serving as inlet and outlet for steam so as to bring the rod to the required temperature. Through the central small hole, a thermometer T is inserted to measure the temperature of the rod. The end D of the rod rests against a rigid support while the other end C touches the tip of the screw of a spherometer supported in another brass pillar in such a manner that the screw and the rod are in the same straight

line. The rod is, thus free to expand only towards C . To detect the exact contact of the screw with the end C of the rod, a galvanometer G , and a cell C are connected through key K as shown.

The length of the rod CD is measured as accurately as possible with the help of a metre scale at room temperature. It is then placed in position in the jacket tube and the temperature indicated by the thermometer is noted. The key K is inserted and the spherometer screw is moved gradually till the galvanometer gives a sudden deflection. The reading of the spherometer is then noted. Now the screw is turned back and the steam is allowed to enter the inlet tube I . After playing round the rod CD , the steam escapes through the outlet tube O . The temperature of the rod CD goes on rising, as indicated by thermometer T and finally becomes constant. After waiting for some time, to ensure that the rod has attained a constant temperature throughout, the spherometer screw is again moved to touch the end C and the reading is noted in a similar manner. The final reading is repeated again and again till it is constant. The difference between these two readings of the spherometer gives the **increase in length** of the rod for the rise of temperature during the experiment. The co-efficient of linear expansion is calculated by using the formula

$$\alpha = \frac{\text{change in length}}{\text{original length} \times \text{rise in temp.}} = \frac{\Delta L}{L \times (100 - t)}$$

ΔL = change in length of the rod.
 L = original length of the rod at room temperature $t^\circ\text{C}$

and $(100 - t)$ is the rise in temperature.

1.9. Comparator Method. This is a standard, precise and a direct method employed for determining the coefficient of thermal expansion when the specimen is in the form of a bar, rod, wire or tube. The principle involved may be stated as follows :

“Two fine marks are made on the experimental rod. A standard rod, one metre long and maintained at a constant temperature is used to measure the distance between these two marks of the experimental rod which varies as the rod expands. Two microscopes provided with micrometer eye-pieces or micrometer screws are used in the comparative estimation of expansion. Hence the method is known as **Comparator Method**.”

The rod under test with two fine marks, AA at a certain distance apart and a standard metre are mounted horizontally in two double-walled troughs, arranged parallel to each other. The troughs are fixed on a platform running on rails, so that either the rod or the standard metre can be brought into the field of view of two microscopes mounted vertically in the two massive pillars PP .

To begin with, the troughs are filled with water and melting ice is placed in the space between the double walls. The experimental

rod and standard metre are both allowed to attain the temperature of melting ice 0°C . The standard metre is brought underneath the

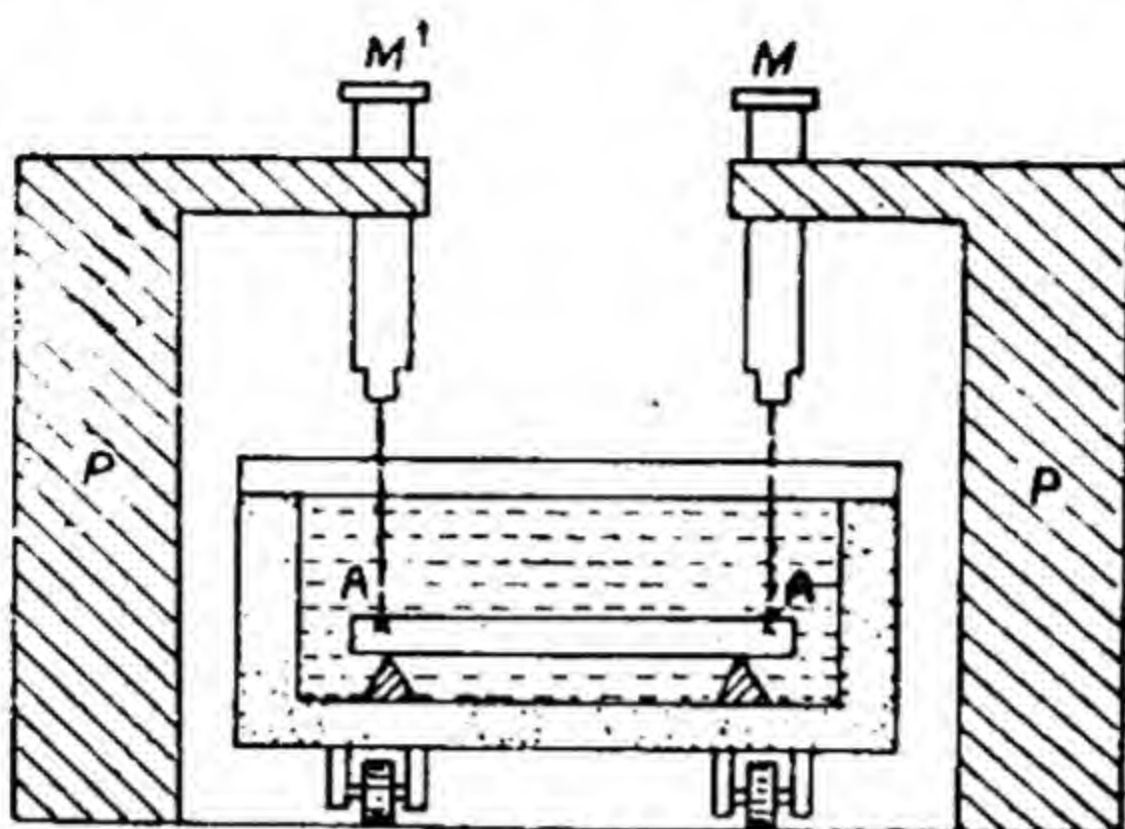


Fig. 1.11.

microscopes. These are adjusted using the micrometer screws until two lines of graduation on the metre, approximately the same distance apart as the marks on the other rod, are in coincidence with their vertical cross-wires. Next, the experimental rod is wheeled into position and the microscopes are set on its marks. From the change in the micrometer readings, the length of the rod at 0°C is readily found out.

Now, the ice cold water in the trough is replaced by water which can be heated under thermostatic control, so that experimental rod can be maintained at any constant temperature. The rod expands and the two microscopes will have to be moved in order to focus the cross-wires of their eye pieces on the two marks once again. The process is repeated for different temperatures so that expansion can be studied over a wide range of temperature. The coefficient of linear expansion can be calculated by applying the relation

$$\alpha = \frac{\Delta L}{L_0 t}$$

where ΔL is the change in length as measured by microscopes
 L_0 = length of the rod at 0°C
 t = rise in temperature.

If the substance is in the form of a tube, the water baths may be dispensed with, and water at constant temperature or steam may be circulated through the inside of the tube.

1.10. Optical Lever Method. (Lavoisier and Laplace's Method). In this method, the expansion of the bar of the material is not measured directly but it is magnified by means of an optical lever. The apparatus is shown in Fig. 1.12. The bar AB under test is clamped at the end A . The free end B touches the vertical rod BO , to the

top of which is attached the telescope at right angles to rod BO . The telescope TT is horizontal and is focussed on a distant vertical scale S . The bar AB is first immersed in ice cold water (0°C) and the scale is observed through the telescope. Let the scale division visible be

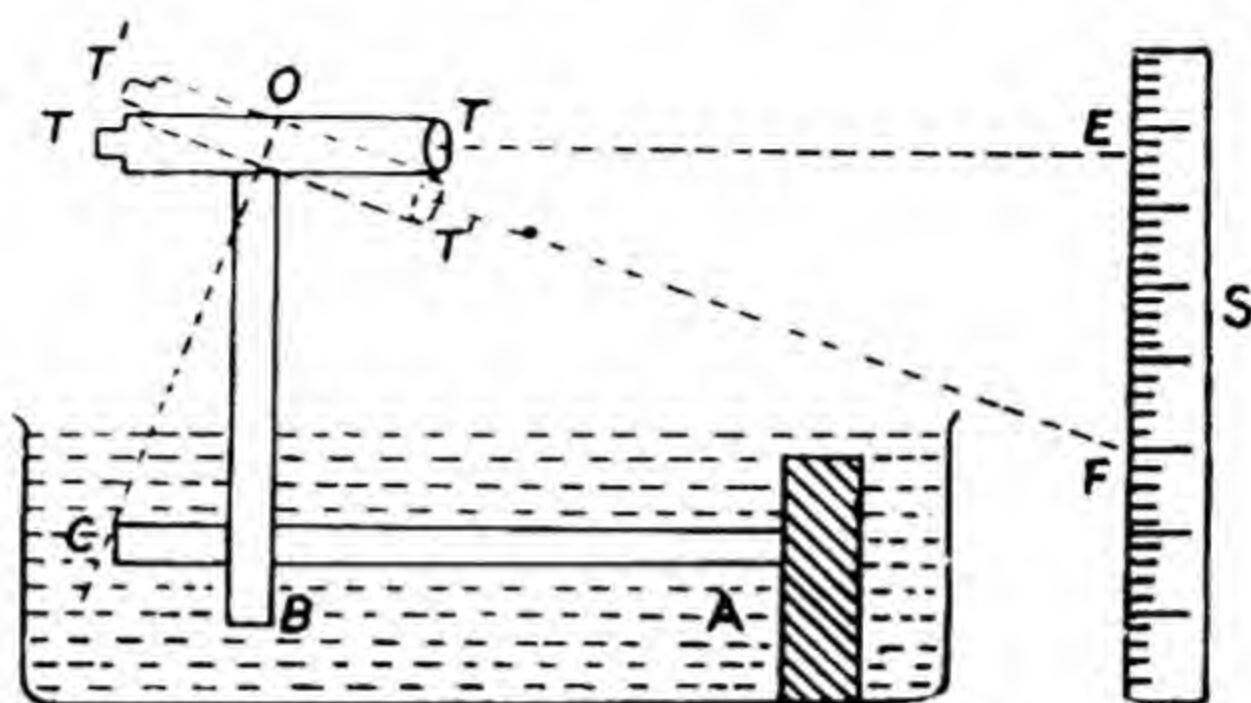


Fig. 1.12.

E . The bar is then enclosed in a constant temperature water bath, which is kept at some known high temperature $t^\circ\text{C}$. The bar expands and the free end B pushes the rod BO at the end B to say C . This causes the telescope to rotate into a position given by $T'T'$, the new scale reading F is then observed through the telescope. The actual small expansion BC of the rod is obtained from the relation,

$$BC = BO \cdot \tan BOC = BO \cdot \tan EOF = BO \times \frac{EF}{OE} = \frac{BO}{OE} \cdot EF$$

Since BO , OE and EF can be measured, BC is determined with fair accuracy by the magnifying device employed.

The coefficient of linear expansion α of the material of the rod is then given by

$$\alpha = \frac{BC}{L \times t} = \frac{BO}{OE} \cdot EF \times \frac{1}{L_0 \times t}$$

Where L_0 is the original length of the rod at 0°C , and t is the temperature of the hot bath.

The same idea may be applied in a simple way by using instead of a telescope a small mirror which can turn about a horizontal axis. As the metal bar expands it turns the mirror through a certain angle θ . A beam of light falls on the mirror and is reflected on to the scale. The reflected beam turns through an angle 2θ . By observing the distance the spot of light moves along the scale, and measuring the distance between scale and mirror, the expansion BC can be calculated.

1.11. Superficial Expansion. Superficial expansion denotes the increase in the surface area on heating. Like the linear expansion the superficial expansion also depends upon

- (i) the original area

- (ii) the rise in temperature and
- (iii) the nature of the material.

If S_0 be the surface area of a metal plate at temperature 0°C , and S_t its surface area at temperature $t^\circ\text{C}$ as shown in Fig 1.13 then, as in the case of linear expansion

$$S_t - S_0 = \beta S_0 t \quad \dots (i)$$

$$\therefore S_t = S_0 + \beta S_0 t = S_0 (1 + \beta t) \quad \dots (ii)$$

where β is a constant depending upon the nature of the material and is known as the **coefficient of superficial expansion**.

\therefore From (i), we have

$$\beta = \frac{S_t - S_0}{S_0 t}$$

Hence the *coefficient of superficial expansion* is defined as the increase in surface area per unit area per degree centigrade rise of temperature.

If S_1 is the area of a surface at a temperature $t_1^\circ\text{C}$ and S_2 at a temperature $t_2^\circ\text{C}$, then

$$S_2 = S_1 [1 + \beta (t_2 - t_1)].$$

1.12. Relation between α and β . Let $ABCD$ be a square metal plate having each side of length l_0 at 0°C . Thus its area at 0°C .

$$S_0 = l_0^2$$

when the metal plate is heated through $t^\circ\text{C}$, the length of each side becomes l_t as shown the Fig. 1.13.

$$\therefore \text{Surface area at } t^\circ\text{C}, S_t = l_t^2 = [l_0(1 + \alpha t)]^2$$

where α is the coefficient of linear expansion.

As already defined, the coefficient of superficial expansion

$$\beta = \frac{S_t - S_0}{S_0 t} = \frac{l_t^2 - l_0^2}{l_0^2 t} = \frac{[l_0(1 + \alpha t)]^2 - l_0^2}{l_0^2 t} = \frac{l_0^2 [(1 + \alpha t)^2 - 1]}{l_0^2 t}$$

$$\therefore \beta = \frac{(1 + \alpha t)^2 - 1}{t} = \frac{1 + \alpha^2 t^2 + 2\alpha t - 1}{t} = \frac{\alpha^2 t^2 + 2\alpha t}{t} = \alpha^2 t + 2\alpha.$$

Since α is small, the value of α^2 can be neglected,
Hence $\beta = 2\alpha$.

This shows that the coefficient of superficial expansion (β) is twice the coefficient of linear expansion (α).

1.13. Cubical expansion. When a body is heated, it expands uniformly in all directions. The increase in its volume is known as the **cubical expansion**. Like the linear and superficial expansions, the cubical expansion also depends upon

- (i) the original volume
- (ii) the rise in the temperature and
- (iii) the nature of the material.

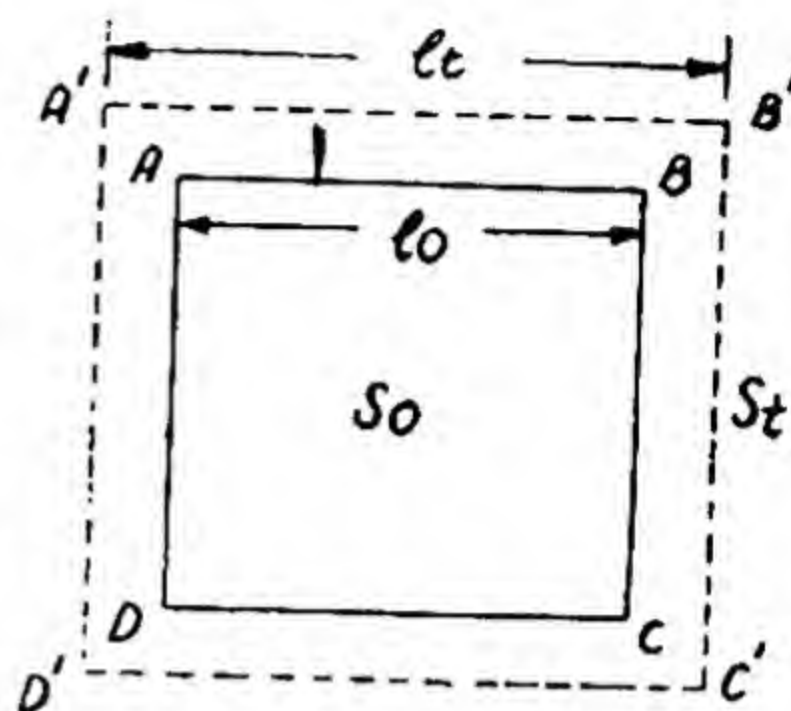


Fig. 1.13.

Let V_o be the volume of a body at 0°C and V_t the volume at some higher temperature. $t^\circ\text{C}$ as shown in the Fig. 1.14 then change in volume

$$V_t - V_o = \gamma V_o t \quad \dots(i)$$

$$\text{or } V_t = V_o(1 + \gamma t)$$

where γ is a constant depending upon the nature of material and is known as the **coefficient of cubical expansion** of the material of the body.

From (i) we have

$$\gamma = \frac{V_t - V_o}{V_o t} \quad \dots(ii)$$

Therefore, the **coefficient of cubical expansion** is defined as the increase in volume per unit volume per degree centigrade rise of temperature.

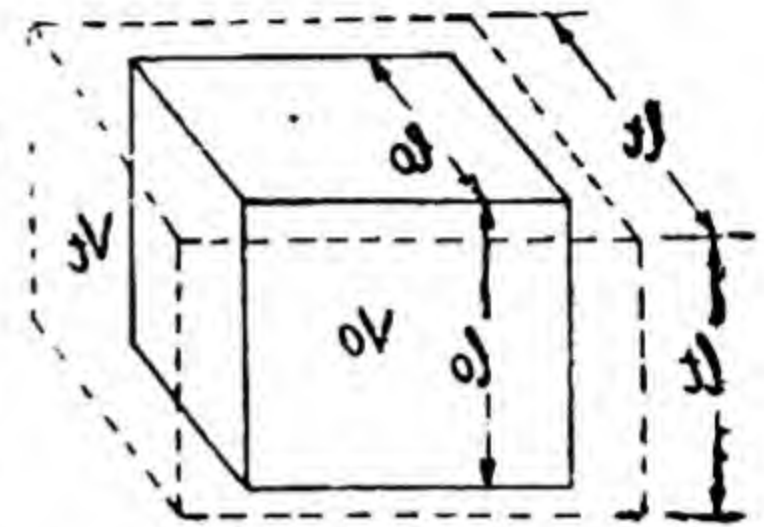


Fig. 1.14.

1.14. Relation between α and γ . Consider a cube of side l_o at temperature 0°C , then its volume at 0°C .

$$V_o = l_o^3$$

Let it now be heated to $t^\circ\text{C}$ so that each of its side becomes l_t as shown in Fig. 1.14 and its volume becomes $V_t = l_t^3 = [l_o(1 + \alpha t)]^3$

We have

$$\begin{aligned} \gamma &= \frac{V_t - V_o}{V_o t} = \frac{l_t^3 - l_o^3}{l_o^3 t} = \frac{[l_o(1 + \alpha t)]^3 - l_o^3}{l_o^3 t} \\ &= \frac{l_o^3[(1 + \alpha t)^3 - 1]}{l_o^3 t} = \frac{(1 + \alpha t)^3 - 1}{t} \\ &= \frac{(1 + \alpha^3 t^3 + 3\alpha t + 3\alpha^2 t^2 - 1)}{t} \\ &= \alpha^3 t^2 + 3\alpha + 3\alpha^2 t \end{aligned}$$

Since α is small, the terms involving α^2 and α^3 can be neglected, so that

$$\gamma = 3\alpha.$$

This shows that the coefficient of cubical expansion is three times the coefficient of linear expansion.

1.15. Change of density with temperature. We know that

$$\text{Density } \rho = \frac{\text{Mass}}{\text{Volume}} = \frac{M}{V}$$

Hence, as the volume of a substance increases on heating and the mass remains constant its density decreases as the temperature is raised.

Let a given substance of mass M be heated from 0°C to $t^\circ\text{C}$. There is no change in the mass M , but its volume changes from V_0 at 0°C to V_t at $t^\circ\text{C}$ and density from ρ_0 to ρ_t . Thus we have from definition.

$$\rho_0 = \frac{M}{V_0} \text{ and } \rho_t = \frac{M}{V_t}$$

$$\therefore \frac{\rho_0}{\rho_t} = \frac{V_t}{V_0} = \frac{V_0(1+\gamma t)}{V_0} = 1+\gamma t.$$

$$\therefore \rho_0 = \rho_t (1+\gamma t) \quad \dots(i)$$

(Note. Density decreases with rise of temperature.)

$$\text{Hence } \gamma = \frac{\rho_0 - \rho_t}{\rho_t \cdot t}.$$

The above equation gives us the relation between coefficient of cubical expansion γ and density, when the temperature rise from 0°C to $t^\circ\text{C}$. If the temperature rises from $t_1^\circ\text{C}$ to $t_2^\circ\text{C}$ and ρ_{t_1} and ρ_{t_2} are the densities at t_1° and $t_2^\circ\text{C}$ respectively, then from equation (i) we have

$$\rho_0 = \rho_{t_1} (1+\gamma t_1) \quad \dots(ii)$$

$$\text{and } \rho_0 = \rho_{t_2} (1+\gamma t_2) \quad \dots(iii)$$

$$\therefore \rho_{t_1} (1+\gamma t_1) = \rho_{t_2} (1+\gamma t_2)$$

$$\text{or } \rho_{t_1} + \rho_{t_2} \gamma t_1 = \rho_{t_2} + \rho_{t_2} \gamma t_2$$

$$\text{or } \rho_{t_1} - \rho_{t_2} = \gamma (\rho_{t_2} t_2 - \rho_{t_1} t_1)$$

$$\therefore \gamma = \frac{\rho_{t_1} - \rho_{t_2}}{(\rho_{t_2} t_2 - \rho_{t_1} t_1)}$$

Hence knowing the densities of a substance at two different temperatures t_1 and t_2 , the value of γ (coefficient of cubical expansion) can be determined indirectly.

1.16. Effect of Temperature on the Physical Properties of solids. In the preceding sections, we have considered the expansion in length, area and volume of solids. In addition to these, there are many other properties of a solid which change with temperature.

1. Density. (ρ). It has been proved in Art 1.15 that $\rho_0 = \rho_t (1+\gamma t)$

Where ρ_0 and ρ_t are the densities of the body at 0°C and $t^\circ\text{C}$. respectively and γ the coefficient of cubical expansion.

2. Moment of Inertia (I). The moment of inertia of a body depends upon its mass and its dimensions. If the body is heated, its mass will remain constant, but its dimensions will in general increase, consequently the moment of inertia will increase. A

familiar example of this fact is afforded by the balance wheel of a watch which has to be compensated against this increase in its moment of inertia.

3. Elasticity. The variation of elasticity with temperature does not yield readily to theoretical treatment, but experimental investigations show that in general it decreases with rise in temperature.

1.17. Expansion of anisotropic solids. In the case of crystalline substances the expansion due to heat is usually different in different directions. Such a body is called *non-isotropic*. In every crystal there can be found three mutually perpendicular directions such that if a cube of a crystal is cut with its edges parallel to the directions, then on heating, the angles will still remain right angles although the lengths of the sides will change unequally. These three directions are called principal axes of dilation of the crystal and the linear coefficients of expansion along these directions are called the principal coefficients of expansion and may be represented by α_x , α_y and α_z .

Consider a cube having initial volume V_0 and initial length of side l_0 .

$$\text{Then } V_0 = l_0^3$$

After heating, the new volume V will be given by

$$\begin{aligned} V &= [l_0 (1 + \alpha_x t)] [l_0 (1 + \alpha_y t)] [l_0 (1 + \alpha_z t)] \\ &= l_0^3 (1 + \alpha_x t) (1 + \alpha_y t) (1 + \alpha_z t) \\ &= V_0 [1 + (\alpha_x + \alpha_y + \alpha_z) t] \end{aligned}$$

Thus we see that for an anisotropic crystal, the coefficient of cubical expansion γ will approximately be given by

$$\gamma = \alpha_x + \alpha_y + \alpha_z$$

i.e., The coefficient of cubical expansion of such a crystal is given by the algebraic sum of the three linear coefficients.

Note. In some crystals, one of the coefficients may be negative.

Isotropic bodies are those whose properties are the same in all the directions e.g. metals, glass, rock salt etc. Expansion of such bodies on heating is the same in all directions.

Example 10. A circular hole 10 cms. in diameter has been cut in a copper plate at a temperature of 75°C . Find the increase in area of the hole when the temperature of the plate becomes 125°C . The value of α for copper $= 16.6 \times 10^{-6}$ per $^\circ\text{C}$.

The area of a surface S_2 at a temperature t_2 $^\circ\text{C}$ is given by

$$S_2 = S_1 [1 + \beta (t_2 - t_1)]$$

where S_1 is the area at temperature t_1 °C

∴ Increase in area = $S_2 - S_1$

Now
$$S_1 = \pi \times \frac{10}{2} \times \frac{10}{2} \text{ sq. cms.}$$

and $\beta = 2\alpha = 2 \times 16.6 \times 10^{-6} \text{ per } ^\circ\text{C.}$

$$\begin{aligned} \therefore S_2 - S_1 &= \frac{\pi}{4} 10^2 \times 2 \times 16.6 \times 10^{-6} \times (125^\circ - 75^\circ) \\ &= \frac{\pi}{4} 10^2 \times 2 \times 16.6 \times 10^{-6} \times 50 \\ &= 0.13 \text{ sq. cm.} \end{aligned}$$

Example 11. If the volume of a block of metal changes by 0.12% when it is heated through 20°C, what is the co-efficient of linear expansion of the metal?

The volume at t °C is given by

$$V_t = V_0 (1 + \gamma t)$$

or
$$\gamma = \frac{V_t - V_0}{V_0 \gamma t}$$

Now
$$\frac{V_t - V_0}{V_0} = 0.12\% = 0.0012$$

Change in temperature $t = 20^\circ$

$$\therefore \gamma = \frac{0.0012}{20} = 0.00006$$

But $\gamma = 3\alpha$

$$\begin{aligned} \therefore \alpha &= \frac{\gamma}{3} = \frac{0.00006}{3} \\ &= 0.00002/^\circ\text{C} \end{aligned}$$

Example 12. Density of a substance at 0°C is 8.92 and at 80°C is 8.80. Calculate the coefficient of its linear expansion.

Density at 0°C, $\rho_0 = 8.92$

Density at 80°C, $\rho_{80} = 8.80$

Using the relation $\rho_0 = \rho_t (1 + \gamma t)$ we have

$$\frac{\rho_0}{\rho_t} = 1 + \gamma t = 1 + \gamma 80$$

or
$$\frac{8.92}{8.80} = 1 + 80\gamma$$

$$\begin{aligned}\text{or} \quad \gamma &= \left(\frac{8.92}{8.80} - 1 \right) \times \frac{1}{80} \\ &= \frac{0.12}{8.80} \times \frac{1}{80}\end{aligned}$$

$$\text{or} \quad \gamma = 0.00017045$$

$$\text{But} \quad \gamma = 3\alpha$$

$$\begin{aligned}\therefore \quad \alpha &= \frac{\gamma}{3} = \frac{0.00017045}{3} \\ &= 0.00005682\end{aligned}$$

Example 13. A piece of a certain metal weighs 50.5 gms. in air 46.0 gms. when immersed in a liquid at 10°C and 46.38 gms. at 45°C . Find the coefficient of cubical expansion of the liquid if the coefficient of linear expansion of the metal is 2×10^{-5} per $^\circ\text{C}$.

$$\text{Loss of weight at } 10^\circ\text{C} = 50.5 - 46 = 4.5 \text{ gms.}$$

$$\text{Loss of weight at } 40^\circ\text{C} = 50.5 - 46.08 = 4.42 \text{ gms.}$$

By Archimedes principle, we have

$$\text{Loss in weight} = \text{Volume of the metal} \times \text{density of the liquid}$$

$$4.5 = V_{10} \rho_{10}$$

and

$$4.42 = V_{40} \rho_{40}$$

\therefore

$$\frac{\rho_{10}}{\rho_{40}} = \frac{4.5}{4.42} \times \frac{V_{40}}{V_{10}} \quad \dots(i)$$

But

$$V_{40} = V_{10} [1 + \gamma(t_2 - t_1)]$$

or

$$\frac{V_{40}}{V_{10}} = 1 + \gamma(40 - 10) = 1 + 30\gamma$$

But

$$\gamma = 3\alpha$$

\therefore

$$\begin{aligned}\frac{V_{40}}{V_{10}} &= 1 + 30 \times 3\alpha \\ &= 1 + 30 \times 3 (2 \times 10^{-5})\end{aligned}$$

\therefore Substituting in (i), we have

$$\begin{aligned}\frac{\rho_{10}}{\rho_{40}} &= \frac{4.5}{4.42} \times (1 + 90 \times 2 \times 10^{-5}) \\ &= 1.02 \times 1.0018 \quad \dots(ii)\end{aligned}$$

But

$$\begin{aligned}\rho_{10} &= \rho_{40} [1 + \gamma(t_2 - t_1)] \\ &= \rho_{40} (1 + \gamma \times 30)\end{aligned}$$

\therefore

$$\frac{\rho_{10}}{\rho_{40}} = 1 + 30\gamma \quad \dots(iii)$$

Equating (ii) and (iii), we have

$$\therefore +30\gamma = 1.02 \times 1.0018$$

$$\therefore \gamma = \frac{1.02 \times 1.0018 - 1}{30} \approx \frac{1.05 - 1}{30} = \frac{0.05}{30} \\ = 1.66 \times 10^{-3}$$

Example 14. A hollow cylindrical vessel is heated through a given range of temperature. Show that the increase in volume is the same as it would be for a solid cylinder of the same dimensions composed of the same substance and heated through the same range of temperature.

(i) **Hollow cylinder**

Let R_1 and l_1 be the radius and length of the cylinder at $t_1^\circ\text{C}$ and R_2 and l_2 the radius and length at $t_2^\circ\text{C}$. If α is the coefficient of linear expansion, then we have

$$R_2 = R_1[1 + \alpha(t_2 - t_1)]$$

and $l_2 = l_1(1 + \alpha(t_2 - t_1))$

Volume $V_1 = \pi R_1^2 l_1$

$$V_2 = \pi R_2^2 l_2$$

$$\therefore V_2 = \pi [R_1(1 + \alpha(t_2 - t_1))]^2 [l_1(1 + \alpha(t_2 - t_1))] \\ = \pi R_1^2 l_1 [(1 + \alpha(t_2 - t_1))]^3 \\ = \pi R_1^2 l_1 [1 + 3\alpha(t_2 - t_1)]$$

(approx).

But $V_1 = \pi R_1^2 l_1$

and $\gamma = 3\alpha$

$$\therefore V_2 = V_1(1 + \gamma(t_2 - t_1))$$

$$\therefore \text{Change in volume} = V_2 - V_1 = V_1\gamma(t_2 - t_1)$$

(ii) **Solid Cylinder**

The change in volume for the rise of temperature from $t_1^\circ\text{C}$ to $t_2^\circ\text{C}$ is given by

$$V_2 - V_1 = V_1\gamma(t_2 - t_1)$$

This is the same as for hollow cylinder calculated above.

Example 15. The volume of the bulb of a mercury thermometer at 0°C is V_0 c.c. and the cross-section of the capillary is A_0 sq. cm. The coefficient of linear expansion of glass is α_g per $^\circ\text{C}$ and the cubical-expansion of mercury γ_m per $^\circ\text{C}$. If the mercury fills the bulb at 0°C , what is the length of the mercury in the capillary at $t^\circ\text{C}$.

(A.M.I.E.)

V_0 = volume of the bulb or that of mercury at 0°C .
When the bulb is heated to $t^\circ\text{C}$ both the bulb as well as mercury in

it expand according to their coefficients of expansion.

Let V_b = Volume of the bulb at $t^\circ\text{C}$
 V_m = Volume of the mercury at $t^\circ\text{C}$.
 $\therefore V_b = V_o(1 + \gamma_g t)$ c.c.
 and $V_m = V_o(1 + \gamma_m t)$ c.c.

The volume of mercury that will be expelled out of the bulb when heated to $t^\circ\text{C}$. is

$$V_m - V_b = V_o(1 + \gamma_m t) - V_o(1 + \gamma_g t) \\ = V_o(\gamma_m - \gamma_g)t$$

Now if A_o = cross-section of the capillary tube at 0°C its value at $t^\circ\text{C}$.

$$A_t = A_o(1 + \beta t)$$

If l is the length of the mercury column at $t^\circ\text{C}$, then

$$l A_t = l A_o(1 + \beta t) = l A_o(1 + 2\alpha_g t) \text{ where } \beta = 2\alpha_g$$

$$\therefore l A_t = V_o(\gamma_m - \gamma_g)t$$

or
$$l = \frac{V_o}{A_t} (\gamma_m - \gamma_g) t$$

$$l = \frac{V_o(\gamma_m - \gamma_g)t}{(1 + 2\alpha_g t)}$$

1.18. Thermal Stresses. When the temperature of a body is raised or lowered, there is corresponding increase or decrease in its dimensions, and if this change in dimensions due to the temperature variation is prevented by the application of external forces etc. the body develops stresses in it which are called **Thermal Stresses**. The corresponding strains due to thermal stresses are called the **thermal strains**.

Suppose a bar of uniform section and of length l is heated through a temperature T . The length of the bar will increase, depending upon the coefficient of linear expansion.

$$\delta l = \text{Extension of the bar when free to expand} = \alpha T l$$

where l = original length of the bar.

α = Coefficient of linear expansion

Now suppose this extension due to increase of temperature is prevented by either fixing the bar at its ends or by the application of external compressive forces.

$$\therefore \text{Thermal strain produced} = \frac{\text{Extension prevented}}{\text{original length}}$$

$$\frac{\delta l}{l} = \frac{\alpha T l}{l} = \alpha T$$

$$\begin{aligned}\text{Thermal stress} &= \text{Thermal strain} \times E \\ &= E\alpha T\end{aligned}$$

$$\text{Hence total Force} = E\alpha T A$$

where A = area of cross section of the bar and

E = young's modulus of elasticity of the material of the bar.

If the bodies are allowed to expand or contract freely with the rise or fall of temperature, no stresses will be developed in the body.

Also the contraction caused by lowering of temperature can be checked by applying tensile forces to the bar resulting in thermal stresses in it.

It should be remembered that (i) when a bar is heated and its expansion is prevented the stress set up in the material of the bar is **compressive** and (ii) when a bar is cooled and its contraction is prevented the stress set up in the material of the bar is **tensile**.

Example 16. The rails of a tramway are welded together at 10°C . Calculate the stresses produced in the rails when heated by sun to 45°C . Given that

Coefficient of linear expansion for steel $= 12.5 \times 10^{-6}/^\circ\text{C}$.

Young's modulus of steel $= 2100 \text{ Tonnes/cm}^2$.

$$\begin{aligned}\text{Thermal strain } \frac{\delta l}{l} &= \alpha T = 12.5 \times 10^{-6} \times (45 - 10) \\ &= 0.0004375\end{aligned}$$

$$\begin{aligned}\therefore \text{Thermal stress} &= E \times \text{strain} = 2100 \times 0.0004375 \\ &= 0.91875 \text{ Tonnes/sq.cm.}\end{aligned}$$

Example 17. A steel wire 1 mm. in diameter is just stretched between two fixed points at a temperature of 25°C . Determine the tension when the temperature falls to 15°C . Given that

Coefficient of linear expansion for steel $= 0.000011/^\circ\text{C}$.
and young's modulus for steel $= 2.14 \times 10^6 \text{ kgm/m}^2$.

$$\text{Thermal strain} = \frac{\delta l}{l} = \frac{l\alpha T}{l} = \alpha T$$

$$\therefore \text{Thermal stress} = E.\alpha T$$

$$\text{Tension (Force)} = F = E.A.\alpha T \text{ kgm.}$$

$$\begin{aligned}&= 2.14 \times 10^6 \pi/4 (0.1)^2 \times 0.000011 \times \\ &\quad (25 - 15) \\ &= 1.82 \text{ kgm.}\end{aligned}$$

Example 18. An underground pipe line is laid in spring at 15°C . What stress would be produced in it when the temperature falls down to -2°C in winter and the pipe line is unable to contract. The coefficient of linear expansion of the pipe $= 0.000012/^{\circ}\text{C}$ and $E = 2 \times 10^6 \text{ kgm/cm}^2$.

$$\text{Thermal strain} = \frac{\alpha T l}{l} = \alpha T$$

$$\begin{aligned} \therefore \text{Thermal stress produced} &= \alpha T E \\ &= 0.000012 \times [15 - (-2)] \times 2 \times 10^6 \\ &= 408 \text{ kgm./cm}^2 \end{aligned}$$

Expected Questions

1. Define the coefficient of linear expansion. Describe how it is experimentally determined. Mention a few cases where you meet this phenomenon in engineering practice. (A.M.I.E.)

2. What happens to a solid when heat is applied to it, if

- (i) it is isotropic
- (ii) it is anisotropic.

How is this effect made use of in

- (a) a metallic thermostat
- (b) sealing a wire in glass
- (c) rivetting of boiler plates
- (d) a clock pendulum.

(A.M.I.E.)

3. What is the relationship between the coefficient of linear expansion and (i) superficial expansion (ii) cubical expansion of a homogenous medium. (A.M.I.E.)

4. What action is taken to compensate for the effect of heat on railway track, gas or water mains, iron bridges, pendulums of clocks and balance wheels of watches. (A.M.I.E.)

5. Explain the working of toluene thermostat and vapour pressure operated thermostat used in refrigerators.

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CHAPTER II

EXPANSION OF LIQUIDS

2.1. Expansion of liquids. Like solids, liquids when heated also expand. As the liquids always take the shape of the vessel in which they are placed, it is quite meaningless to speak of their linear and superficial expansions. It is the increase in volume which they suffer when heated and thus, they have got only cubical expansion. Hence in the case of liquids only cubical expansion is measured.

2.2. Apparent expansion. To heat a liquid it has to be contained in some vessel. When the liquid is heated the containing vessel also expands simultaneously although the expansion of the latter is smaller than that of the former. If the expansion of the containing vessel is not considered then the observed expansion is called the apparent expansion of the liquid.

The coefficient of apparent expansion (γ_a) of a liquid is the ratio of the apparent increase in volume per degree centigrade rise in temperature to the original volume of the liquid at 0°C .

$$\therefore \gamma_a = \frac{\text{Apparent (observed) increase in volume}}{\text{Original Volume} \times \text{rise in temperature}} = \frac{V_t - V_o}{V_o t}$$

$$\text{or } V_t = V_o (1 + \gamma_a t)$$

where V_o and V_t are the observed volumes of the liquid at 0°C and $t^\circ\text{C}$ and t is the rise in temperature.

2.3. Real Expansion. If the expansion of the containing vessel is taken into account, the expansion is called the **real expansion**.

The coefficient of real expansion (γ_r) of a liquid is the ratio of the real increase in volume per degree centigrade rise of temperature to the original volume of the liquid at 0°C .

$$\therefore \gamma_r = \frac{\text{Real increase in volume}}{\text{Original volume} \times \text{rise in temperature}} = \frac{V_t - V_o}{V_o t}$$

$$\text{or } V_t = V_o (1 + \gamma_r t)$$

where V_0 and V_t are the volumes of the liquid at 0°C and $t^\circ\text{C}$ and t is the rise in temperature above 0°C .

Note. The coefficient of real expansion (γ_r) is also called as the coefficient of absolute expansion.

Hence in the case of liquids, two expansions, real and apparent have to be considered. The real or true expansion of the liquid is greater than the apparent expansion since it also takes into account the expansion of the vessel.

Table for the coefficient of real expansion γ_r

Substance	γ_r per $^\circ\text{C}$	Substance	γ_r per $^\circ\text{C}$
Alcohol	0.00108	Olive oil	0.0007
Benzene	0.00114	Paraffin oil	0.0009
Glycerine	0.00053	Pentane	0.00159
Water	0.00015	Toluene	0.00109
Mercury	0.00018	Turpentine oil	0.00095

2.4. Relation between Co-efficient of real and apparent expansions.

The real expansion of a liquid is always greater than the apparent expansion. To show this experimentally, take a glass flask with a long narrow neck and fill it with coloured water upto the mark A . Now suddenly put this flask into hot water contained in a trough. It will be observed that the level of the liquid falls in the first instance to B and then slowly rises to C . This is because of the fact that when the flask is immersed in hot water, it first takes the heat from the hot water and expands. Therefore, the level of the liquid falls to B . Thereafter the liquid expands and the expansion of the liquid also being greater than that of the vessel its level ultimately rises to C from B . In fact, we observe the expansion from A to C . Thus it is clear that

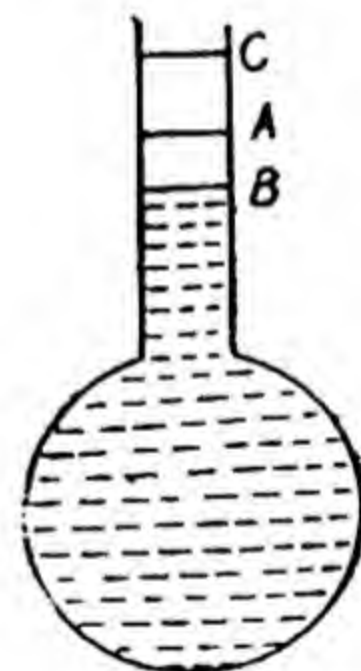


Fig. 2.1

- (i) Volume of the portion AC measures the apparent expansion.
- (ii) Volume of the portion BC measures the real or true expansion of the liquid.
- (iii) Volume of the portion AB measures the expansion of the vessel for a given rise of temperature.

Hence Real expansion

$$BC = \text{Apparent expansion } (AC) + \text{Expansion of the vessel } (AB) \quad \dots(i)$$

$$\text{or } BC = AC + AB$$

Let us suppose the volume of the liquid up to A is equal to V . Let γ_r and γ_a represent the coefficients of real and apparent expansions

of the liquid. γ_g is the coefficient of cubical expansion of glass and $t^\circ C$ is the rise of temperature, then

Real expansion $BC = \gamma_r \times V \times t$

Apparant expansion $AC = \gamma_a \times V \times t$

Expansion of vessel $AB = \gamma_g \times V \times t$

Substituting in (i), we have

$$\gamma_r V \times t = \gamma_a V \times t + \gamma_g V \times t$$

$$\therefore \gamma_r = \gamma_a + \gamma_g$$

or Coefficient of real expansion of a liquid

= Coefficient of apparent expansion of the liquid

+ Coefficient of cubical expansion of the material of the vessel.

2.5. Effect of temperature on the density of a liquid. Whenever a liquid is heated, there is a change in the density of the liquid. Consider a mass M of a liquid and let ρ_0 and ρ_t be the values of its density at temperatures $0^\circ C$ and $t^\circ C$ respectively.

Since the mass remains constant, the volumes of the liquid V_0 and V_t at temperatures $0^\circ C$ and $t^\circ C$, respectively are given by

$$V_0 = \frac{M}{\rho_0}$$

and

$$V_t = \frac{M}{\rho_t}$$

\therefore

$$\frac{V_t}{V_0} = \frac{\rho_0}{\rho_t}$$

But

$$V_t = V_0 (1 + \gamma_r t)$$

where

γ_r = coefficient of real expansion of the liquid.

\therefore

$$\frac{V_t}{V_0} = 1 + \gamma_r t = \frac{\rho_0}{\rho_t}$$

\therefore

$$\rho_0 = \rho_t (1 + \gamma_r t)$$

2.6. Determination of Coefficient of Apparent expansion (γ_a). The coefficient of apparent expansion of a liquid can be determined by any of the following methods.

- (i) The volume thermometer or Dilatometer method.
- (ii) The Weight thermometer method.
- (iii) The hydrostatic or Sinker method.

- (i) **The volume thermometer or dilatometer method.** A dilatometer consists of a bulb blown at the lower end of a thermometer tubing as shown. The volume of the bulb and the volume of each division of the stem are first determined. The experimental liquid is filled in the dilatometer after which it is placed in an ice bath. The initial volume (V_0) of the liquid at 0°C is found. The dilatometer is then placed in a bath having a temperature $t^\circ\text{C}$. When the level of the liquid, which falls in the first instance and then rises up, becomes steady, the final volume (V_t) of the liquid is found.



Fig. 2.3.

If V_0 and V_t are the volumes of the liquid at 0°C and $t^\circ\text{C}$ respectively then the increase in volume v can be readily calculated from the known volume corresponding to each division. Thus the coefficient of apparent expansion is given by

$$\gamma_a = \frac{V_t - V_0}{V_0 t} = \frac{v}{V_0 t}$$

$$= \frac{\text{Increase in Volume}}{\text{Original volume} \times \text{rise in temperature}}$$

If the initial temperature is not 0°C but $t_1^\circ\text{C}$ and the final temperature is $t_2^\circ\text{C}$ then,

$$\gamma_a = \frac{V_2 - V_1}{V_1 (t_2 - t_1)}$$

$$= \frac{\text{Increase in Volume}}{\text{Original volume} \times \text{rise in temperature}}$$

Where V_1 is the volume at $t_1^\circ\text{C}$ and V_2 the volume of the same mass of the liquid at $t_2^\circ\text{C}$.

- (ii) **The Weight Thermometer method.** This offers a more accurate method for measuring the coefficient of apparent expansion of a liquid, since it is based on the determination of weight and not volume. It consists of an elongated glass or silver bulb B provided with a bent capillary tube C drawn into a narrow jet at the end as shown in Fig. 2.4. In order to find the coefficient of apparent expansion the bulb is cleaned, dried and weighed when empty. It is then filled with the liquid whose coefficient of apparent expansion is to be determined. The filling is done by the method of alternate heating and cooling of the bulb B and keeping the end of the bent capillary tube always inside the

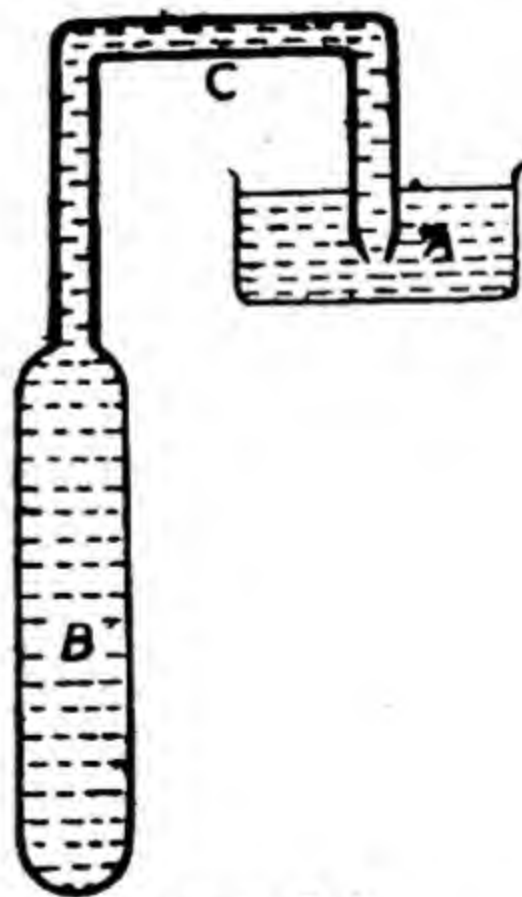


Fig. 2.4.

bulb B and keeping the end of the bent capillary tube always inside the

liquid (to be filled) contained in a beaker *A*. When filled completely, it is placed for some time in a water-bath at the room temperature, keeping the end of the capillary tube still in the liquid in the beaker. It is then removed and carefully dried, any drops of the liquid adhering to the end of *C* are removed by blotting paper and is weighed. The difference of the two masses is the mass of the liquid filling the thermometer at the room temperature $t_1^\circ\text{C}$.

Now the thermometer filled with the liquid is suspended in a water bath in which water is kept at a constant higher temperature $t_2^\circ\text{C}$. The end of the capillary tube is kept outside the hot water bath. As the liquid gets heated, it expands and is expelled out of the thermometer. When no more of the liquid comes out, the liquid has attained a constant temperature of the bath. The thermometer is taken out of the bath, wiped well on its outside and allowed to cool to the room temperature. Its weight is again taken. From the three weighings thus made the coefficient of apparent expansion can be found out as follows.

Let m = the mass of the empty weight thermometer,

m_1 = its mass when filled with liquid at the initial temperature $t_1^\circ\text{C}$.

m_2 = its mass when filled with liquid at the final temperature $t_2^\circ\text{C}$.

$M_1 = m_1 - m$ = mass of the liquid that fills the thermometer at $t_1^\circ\text{C}$.

$M_2 = m_2 - m$ = mass of the liquid that fills the thermometer at $t_2^\circ\text{C}$.

$t = t_2 - t_1$ = the rise in temperature.

Let V_1 and V_2 be the volumes of the weight thermometer and ρ_1 and ρ_2 the densities of the liquid at the initial and final temperatures respectively, γ_r the coefficient of real expansion of the liquid and γ_g the co-efficient of the cubical expansion of the material of the weight thermometer.

From the definition of density, we have.

$$\rho_1 = \frac{M_1}{V_1} \text{ and } \rho_2 = \frac{M_2}{V_2}$$

$$\therefore \frac{M_1}{M_2} = \frac{V_1 \rho_1}{V_2 \rho_2} = \frac{V_1}{V_2} \times \frac{\rho_1}{\rho_2} \quad \dots(i)$$

$$\text{Now } \rho_1 = \rho_2 (1 + \gamma_r t) \text{ or } \frac{\rho_1}{\rho_2} = 1 + \gamma_r t$$

$$\text{and } V_2 = V_1 (1 + \gamma_g t) \text{ or } \frac{V_2}{V_1} = 1 + \gamma_g t$$

Substituting these values in equation (i) we have

$$\frac{M_1}{M_2} = \frac{1 + \gamma_r t}{1 + \gamma_g t}$$

Cross multiplying and simplifying for γ_r , we have

$$\gamma_r = \frac{M_1 - M_2}{M_2 t} + \frac{M_1}{M_2} \gamma_g \quad \dots (ii)$$

A simple example will show that for many liquids it is permissible to put $\frac{M_1}{M_2} = 1$.

From equation (ii) we have

$$\gamma_r = \frac{M_1 - M_2}{M_2 t} + \gamma_g$$

$$\gamma_r - \gamma_g = \frac{M_1 - M_2}{M_2 t}$$

But $\gamma_r - \gamma_g = \gamma_a =$ coefficient of apparent expansion

$$\therefore \text{Coefficient of apparent expansion } \gamma_a = \frac{M_1 - M_2}{M_2 t}$$

$$= \frac{\text{Mass of the liquid expelled}}{\text{Mass of liquid left at higher temp.} \times \text{rise of temp.}}$$

The weight thermometer thus enables, the coefficient of apparent expansion of a liquid to be easily determined. If the coefficient of real expansion of the liquid is required, the coefficient of cubical expansion γ_g of the material of the thermometer must be added to the coefficient of apparent expansion, but this method does not give a very accurate value for the coefficient of real expansion as γ_g is not known to a high degree of accuracy.

If the weight thermometer is made of quartz or silica or pyrex, the magnitude of γ_g would then be so small as to be negligible in comparison with the coefficient of apparent expansion, so by ignoring the expansion of the bulb i.e., by putting $\gamma_g = 0$ in equation (ii) we have

$$\text{Coefficient of real expansion } \gamma_r = \frac{M_1 - M_2}{M_2 t}$$

The advantages of using silica in place of glass for the bulb are

(i) It can withstand fluctuations in temperature.

(ii) Its coefficient of cubical expansion is smaller.

Since weight can be measured with great accuracy, the weight thermometer is preferable to a volume method of measuring expansion. It is, however, not suitable for use with volatile liquids.

Example 1. A weight thermometer contains 101.75 gms. of a liquid at 14°C . On heating it to 100°C , 1.75 gms. of the liquid are expelled. Find the coefficient of absolute expansion of the liquid if the coefficient of linear expansion of glass is 0.000009.

Mass of liquid at 14°C $M_1 = 101.75$ gms.

Mass of liquid expelled $(M_1 - M_2) = 1.75$ gms.

Mass of liquid left behind $M_2 = 101.75 - 1.75 = 100$ gms.

Rise of temperature $(t_2 - t_1) = 100 - 14 = 86^{\circ}\text{C}$

$$\begin{aligned}\therefore \text{Coefficient of apparent expansion } \gamma_a &= \frac{M_1 - M_2}{M_2 \times (t_2 - t_1)} \\ &= \frac{1.75}{100 \times 86} = 2.03 \times 10^{-4}\end{aligned}$$

Coeff. of linear expansion of glass $\alpha = 0.000009$

$$\begin{aligned}\therefore \text{Coeff. of cubical expansion of glass } \gamma_g &= 0.000009 \times 3 \\ &= 0.000027\end{aligned}$$

Hence

$$\begin{aligned}\gamma_r &= \gamma_a + \gamma_g \\ &= 2.03 \times 10^{-4} + 0.27 \times 10^{-4} \\ &= 10^{-4} [2.03 + 0.27] \\ &= 2.3 \times 10^{-4} = 0.00023\end{aligned}$$

Example 2. If the coefficient of apparent expansion of mercury in glass be $\frac{1}{6500}$, what mass of mercury will overflow from a weight thermometer which contains 400 gm. of mercury at 0°C when the temperature is raised to 90°C .

$$\text{Coefficient of apparent expansion } \gamma_a = \frac{1}{6500}$$

But

$$\begin{aligned}\gamma_a &= \frac{\text{mass expelled}}{\text{mass left at higher temp.} \times t.} \\ \gamma_a &= \frac{\text{mass expelled}}{(\text{total mass} - \text{mass expelled}) \times t}\end{aligned}$$

Denoting the mass expelled by x , we have

$$\frac{1}{6500} = \frac{x}{(400 - x) \times 90}$$

$$\text{or } 36000 - 90x = 6500x$$

$$\text{or } x = 5.57 \text{ gms.}$$

Example 3. If a weight thermometer is completely filled with 275 gm. of mercury at 0°C , calculate the mass of mercury which will fill it at 130°C . The coefficient of linear expansion of the material of the weight thermometer being 9×10^{-6} per $^{\circ}\text{C}$ and coefficient of real expansion of mercury is 182×10^{-6} per $^{\circ}\text{C}$.

Co-efficient of linear expansion of the material $= 9 \times 10^{-6}$.

\therefore Coeff. of cubical expansion $\gamma_g = 3 \times 9 \times 10^{-6}$.

Now

$$\begin{aligned}\gamma_a &= \gamma_r - \gamma_g \\ &= 182 \times 10^{-6} - 3 \times 9 \times 10^{-6} \\ &= 155 \times 10^{-6} \text{ per } ^{\circ}\text{C}.\end{aligned}$$

Let M_2 gm. be the mass of mercury which would fill the weight thermometer at 100°C .

\therefore Mass expelled $= (\text{Total mass} - M_2) = (275 - M_2)$

Coeff. of app. expansion $\gamma_a = \frac{\text{mass expelled}}{\text{mass left} \times t} = \frac{275 - M_2}{M_2 \times 100}$

$$\therefore 155 \times 10^{-6} = \frac{275 - M_2}{M_2 \times 100}$$

$$\text{or } 155 \times M_2 \times 10^{-4} = 275 - M_2$$

$$\text{or } M_2(1 + 155 \times 10^{-4}) = 275$$

$$\therefore M_2 = \frac{275}{1 + 155 \times 10^{-4}} = \frac{275}{1.0155} = 269.2 \text{ gms.}$$

Example 4. 45 grams of alcohol are needed to completely fill up a weight thermometer at 15°C . Calculate the weight of the alcohol which will overflow when the weight thermometer is heated to 33°C . Given γ_a for alcohol is 0.00121.

Mass of alcohol completely filling

the weight thermometer at 15°C $M_1 = 45$ gms.

Rise in temperature $t = 33 - 15 = 18^{\circ}\text{C}$.

Let m be the mass of alcohol expelled

\therefore Mass of alcohol left behind $M_2 = (45 - m)$ gm.

$$\text{Hence } \gamma_a = \frac{m}{M_2 \times t} \text{ or } 0.00121 = \frac{m}{(45 - m) \times 18}$$

$$\therefore m = 0.96 \text{ gms.}$$

(iii) **The Hydrostatic or Sinker Method.**

Besides the weight thermometer method, there is a hydrostatic method or Matthiessen's method for determining the coefficient of apparent expansion which utilises **Archimede's principle**.

A sinker which may be a cube or a bulb of glass or silica as shown in fig. 2.5 loaded with lead shots, so that it just sinks in the liquid, is first weighed in air and then weighed when it is totally immersed in the liquid at room temp. $t_1^\circ\text{C}$. The liquid is then heated to a new constant temperature $t_2^\circ\text{C}$, and the new apparent weight of the sinker in the liquid at $t_2^\circ\text{C}$ is again measured. In order to avoid inaccuracy in weighing, the liquid is arranged under the balance case and the sinker is suspended from the balance by a fine wire passing through a hole in the bottom of the case.

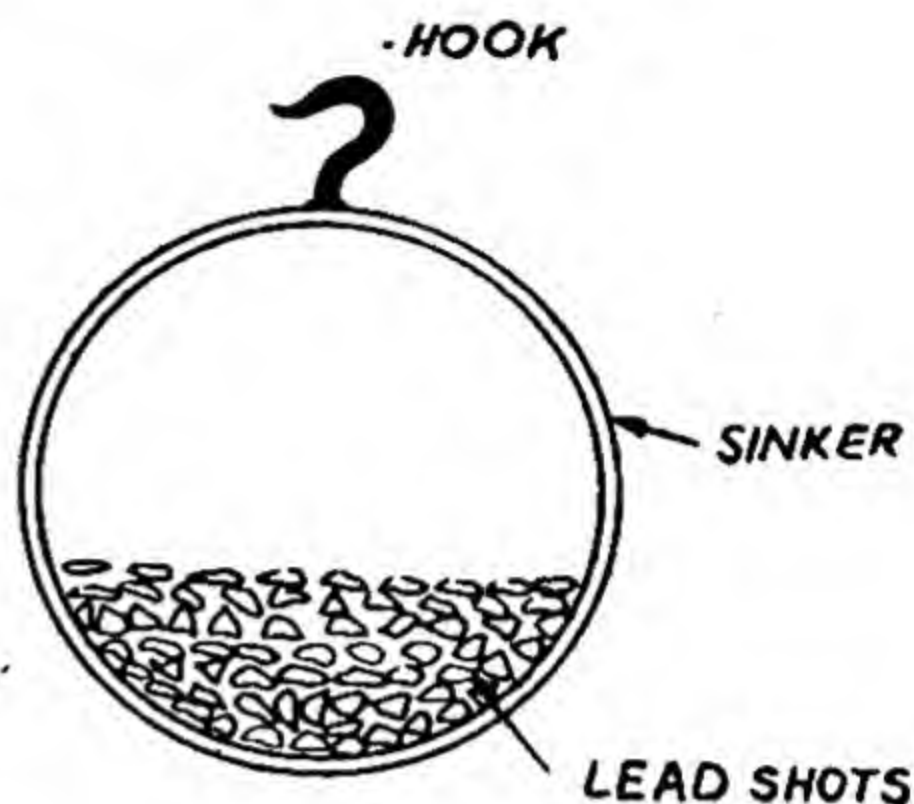


Fig. 2.5.

Suppose m_0 , m_1 and m_2 are the respective weights of the sinker in air, in the liquid at $t_1^\circ\text{C}$, and in the liquid at $t_2^\circ\text{C}$. Now Archimede's principle states that the loss in weight of a body immersed in a liquid is equal to the weight of the liquid displaced by the body. In the present case,

Let $M_1 = m_0 - m_1 = \text{loss in weight of the sinker at the initial temperature } t_1^\circ\text{C}$.

and $M_2 = m_0 - m_2 = \text{loss in weight of the sinker at the final temperature } t_2^\circ\text{C}$.

$t = \text{the difference in final and initial temperature of liquid}$
 $= (t_2 - t_1)$

V_1 and V_2 the volumes of the sinker and ρ_1 and ρ_2 the densities of the liquid at the initial and final temperatures respectively.

$$\therefore \rho_1 = \frac{M_1}{V_1} \text{ and } \rho_2 = \frac{M_2}{V_2}$$

$$\text{or } \frac{M_1}{M_2} = \frac{\rho_1 V_1}{\rho_2 V_2} = \frac{V_1}{V_2} \frac{\rho_1}{\rho_2}$$

$$\text{or } \frac{M_1}{M_2} = \frac{1 + \gamma_r t}{1 + \gamma_g t}$$

Where γ_r is the co-efficient of real expansion of the liquid and γ_g the coefficient of cubical expansion of the material of the sinker.

Cross-multiplying and simplifying for γ_r , we have

$$\gamma_r = \frac{M_1 - M_2}{M_2 t} + \frac{M_1}{M_2} \gamma_g \quad \dots(2)$$

Again putting $\frac{M_1}{M_2} = 1$ (approx.) we have

$$\gamma_r = \frac{M_1 - M_2}{M_2 t} + \gamma_g$$

$$\text{or} \quad \gamma_r - \gamma_g = \frac{M_1 - M_2}{M_2 t}$$

$$\text{or} \quad \gamma_a = \frac{M_1 - M_2}{M_2 t}$$

All the quantities in the expression for the coefficient of apparent expansion have been measured in the experiment and so it can be calculated, but we cannot find the coefficient of real expansion of the liquid unless the cubical expansion of the material of the sinker is known.

Example 5. A piece of glass which weighs 92 gms, in air is found to weigh 51.6 gms. in a liquid at 10°C . At 95°C its apparent weight in the same liquid is 53.9 gm. If the coefficient of cubical expansion of glass is $24 \times 10^{-6}/^\circ\text{C}$ find the coefficient of absolute expansion of the liquid.

Loss of weight at 10°C , $M_1 = 92 - 51.6 = 40.4$ gm.

Loss of weight at 95°C , $M_2 = 92 - 53.9 = 38.1$ gm.

Coefficient of cubical expansion of glass, $\gamma_g = 24 \times 10^{-6}/^\circ\text{C}$.

$$\gamma_a = \frac{M_1 - M_2}{M_2 t} = \frac{40.4 - 38.1}{38.1 \times (95 - 10)}$$

$$= \frac{2.3}{38.1 \times 85} = 0.000715/^\circ\text{C}.$$

$$\gamma_r = \gamma_a + \gamma_g$$

$$= 0.000715 + 0.000024$$

$$= 0.000739$$

Example 6. A piece of solid whose coefficient of linear expansion is α , weighs W gm. in air. It weighs W_1 gm. in water at 0°C and W_2 gm. in water at $t^\circ\text{C}$. Determine the coefficient of absolute expansion of water. (A.M.I.E.)

Loss of weight in water at 0°C , $M_1 = W - W_1$

Loss of weight in water at $t^\circ\text{C}$, $M_2 = W - W_2$

Coefficient of apparent expansion

$$\gamma_a = \frac{M_1 - M_2}{M_2 \times t}$$

$$\gamma_r = \gamma_a + \gamma_g$$

\therefore

$$= \frac{M_1 - M_2}{M_2 t} + 3\alpha$$

$$= \frac{W_2 - W_1}{(W - W_2) t} + 3\alpha.$$

Example 7. A loaded glass bulb weighs 156.25 gms. in air, 57.5 gm. when immersed in a liquid at 15°C and 58.7 gm. when immersed at 52°C . Calculate the mean coefficients of real expansion of the liquid between 15°C and 52°C . Coefficient of linear expansion of glass $= 9 \times 10^{-6}/^\circ\text{C}$:

$$M_1 = W - W_1 = 156.25 - 57.50 \\ = 98.75 \text{ gms.}$$

$$M_2 = W - W_2 = 156.25 - 58.57 \\ = 97.68 \text{ gms.}$$

Rise in temperature $t = 52 - 15 = 37^\circ\text{C}$

$$\gamma_a = \frac{M_1 - M_2}{M_2 t} = \frac{98.75 - 97.68}{97.68 \times 37}$$

$$= \frac{1.07}{97.68 \times 37} = 29.6 \times 10^{-5}$$

But
where

$$\gamma_r = \gamma_a + \gamma_g$$

$$\gamma_g = 3\alpha = 9 \times 10^{-6} \times 3 = 27 \times 10^{-6} \\ = 2.7 \times 10^{-5}$$

\therefore

$$\gamma_r = 29.6 \times 10^{-5} + 2.7 \times 10^{-5} \\ = 32.3 \times 10^{-5} \text{ per } ^\circ\text{C}.$$

2.7. Principle of U-tube for Comparing densities of liquids. In order to compare the densities of two liquids which do not mix with each other, the liquids are poured in the vertical limbs AC and DB of a U-tube. Let the surface of separation of the two liquids be at D. If the height of the liquid of density ρ_1 is h_1 , and that of the other liquid of density ρ_2 is h_2 , above the horizontal line DC, then

$$\text{Pressure at D} = h_1 \rho_1 g + P$$

$$\text{Pressure at C} = h_2 \rho_2 g + P$$

where g is the acceleration due to gravity and P is the atmospheric pressure.

Since the points C and D are in the same horizontal line,

$$\therefore h_1 \rho_1 g + P = h_2 \rho_2 g + P$$

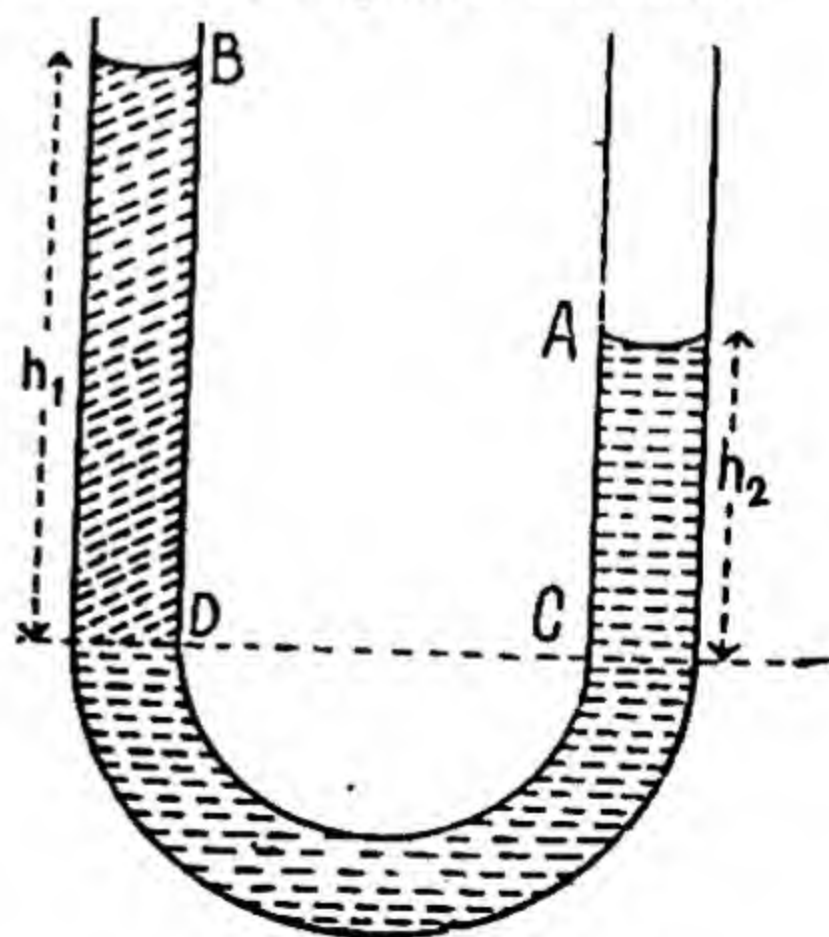


Fig. 6.

or
$$\frac{\rho_2}{\rho_1} = \frac{h_1}{h_2}$$

Thus the heights of the balancing liquid columns are inversely proportional to their densities.

2.8. Measurement of real or absolute expansion of liquids.

The co-efficient of real expansion of a liquid can be determined by the following methods.

- (i) Dulong and Petit's method.
- (ii) Regnault's method.

(i) **Dulong and Petit's method.** It is important to devise a way of finding the coefficient of real expansion of a liquid which is independent of the expansion of the containing vessel. A method for determining the coefficient of real expansion of a liquid in which expansion of the vessel has no effect on the observations, was

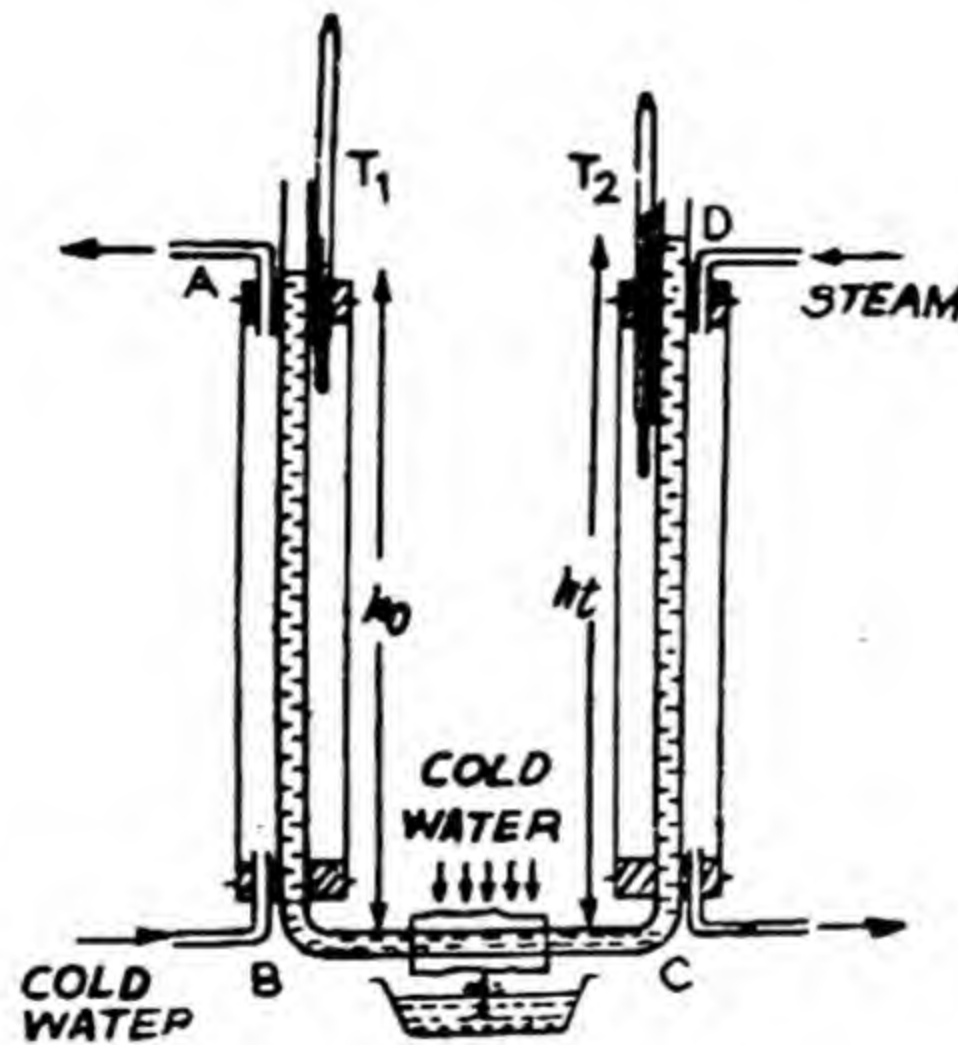


Fig. 2.7.

developed by Dulong and Petit in 1820. The method is based on the famous hydrostatic principle that if two liquid columns balance each other, their heights are inversely proportional to their densities, this relation is independent of the diameter of the tube.

The simple diagram of the apparatus is shown in the Fig. 2.7. It consists of a glass U tube ABCD, the limbs AB and CD are vertical while the portion BC is horizontal. The vertical limbs AB and CD are surrounded by wider glass tubes with their ends closed with corks. Through both the upper and lower corks pass narrow bent tubes which serve the purpose of inlets or outlets. Two thermometers T_1 and T_2 are also inserted through the corks in the two limbs as shown.

The liquid whose coefficient of real expansion is to be determined is filled inside the U-tube so that its level is visible in each limb.

One of the limbs, say AB is kept cold by circulating ice cold water in the outer tube. The water enters at the lower inlet tube and goes out through the upper outlet. The liquid in the limb CD is heated by passing steam in the outer tube. The steam enters from the upper end and leaves at the lower end. Liquid in both the limbs of U-tube is the same, but owing to the difference in temperature, the density of the liquid on the two sides is different. In order to prevent the conduction of heat from the hot to the cold limb, the horizontal portion BC of the tube is covered with cloth over which cold water is constantly poured.

The two limbs and hence liquid in them is thus maintained at different temperatures. The liquid in CD is heated to the temperature of steam and its level rises. When the liquid level in the two limbs becomes stationary and an equilibrium state has been reached, the heights of the liquid level in AB and CD above the axis of the horizontal tube BC are measured and the temperatures in the two limbs are also noted.

Let the temperature of the liquid on the side $AB = 0^\circ C$	
Height of the liquid column in AB	$= h_o$
Temperature of the liquid on the side CD	$= t^\circ C$
Height of the liquid column in CD	$= h_t$
Density of liquid at $0^\circ C$	$= \rho_o$
Density of liquid at $t^\circ C$	$= \rho_t$

The pressure exerted on the horizontal portion of the tube by the cold column is $h_o \rho_o g$ and that by the hot column is $h_t \rho_t g$. As the liquid columns are in equilibrium, the pressure exerted by them in the same horizontal line BC is the same.

$$\therefore h_o \rho_o g = h_t \rho_t g$$

$$\text{or } h_o \rho_o = h_t \rho_t$$

$$\text{or } \frac{\rho_o}{\rho_t} = \frac{h_t}{h_o}$$

$$\text{But } \frac{\rho_o}{\rho_t} = (1 + \gamma_r t) \text{ where } \gamma_r \text{ is the coefficient of}$$

real expansion of the liquid.

$$\therefore 1 + \gamma_r t = \frac{h_t}{h_o}$$

$$\text{or } h_o + h_o \gamma_r t = h_t$$

$$\text{or } h_o \gamma_r t = h_t - h_o$$

$$\text{or } \gamma_r = \frac{h_t - h_o}{h_o t}$$

The above expression is quite independent of the expansion.

of the material of the containing vessel and hence gives us the coefficient of real expansion of the liquid.

Dulong and Petit's experiment, though simple in design, was subject to the following errors.

(i) A small portion of the liquid in each column has to project above its constant temperature bath in order that its height may be read.

(ii) Since surface tension varies with temperature its effect on the two liquid surfaces will be different although this source of error is eliminated to a great extent by making the upper ends of the limbs wide.

(iii) Since the two limbs are at a large distance apart, the small difference in height ($h_t - h_o$) of the two columns cannot be accurately measured, particularly in the case of mercury which has a small coefficient of expansion.

(iv) No efficient stirring arrangement can be used.

To overcome these errors, Regnault modified Dulong and Petit's original method and his apparatus is explained below.

(ii) **Regnault's method.** The apparatus consists of two pieces of glass tubing $ABCD$ and $EFGH$ as shown in Fig. 2.8 joined by a flexible iron tube to allow them to expand independently. The axes of the portions BC of the tube $ABCD$ and of the portion GF of the tube $EFGH$ are kept accurately in the same horizontal plane. The portions HG and AB are enclosed in a wide bore tube. Similarly the portions FE and CD are enclosed in wide bore tubes as shown.

The liquid whose coefficient of real or absolute expansion is to be determined is filled into the tube so that it stands at the

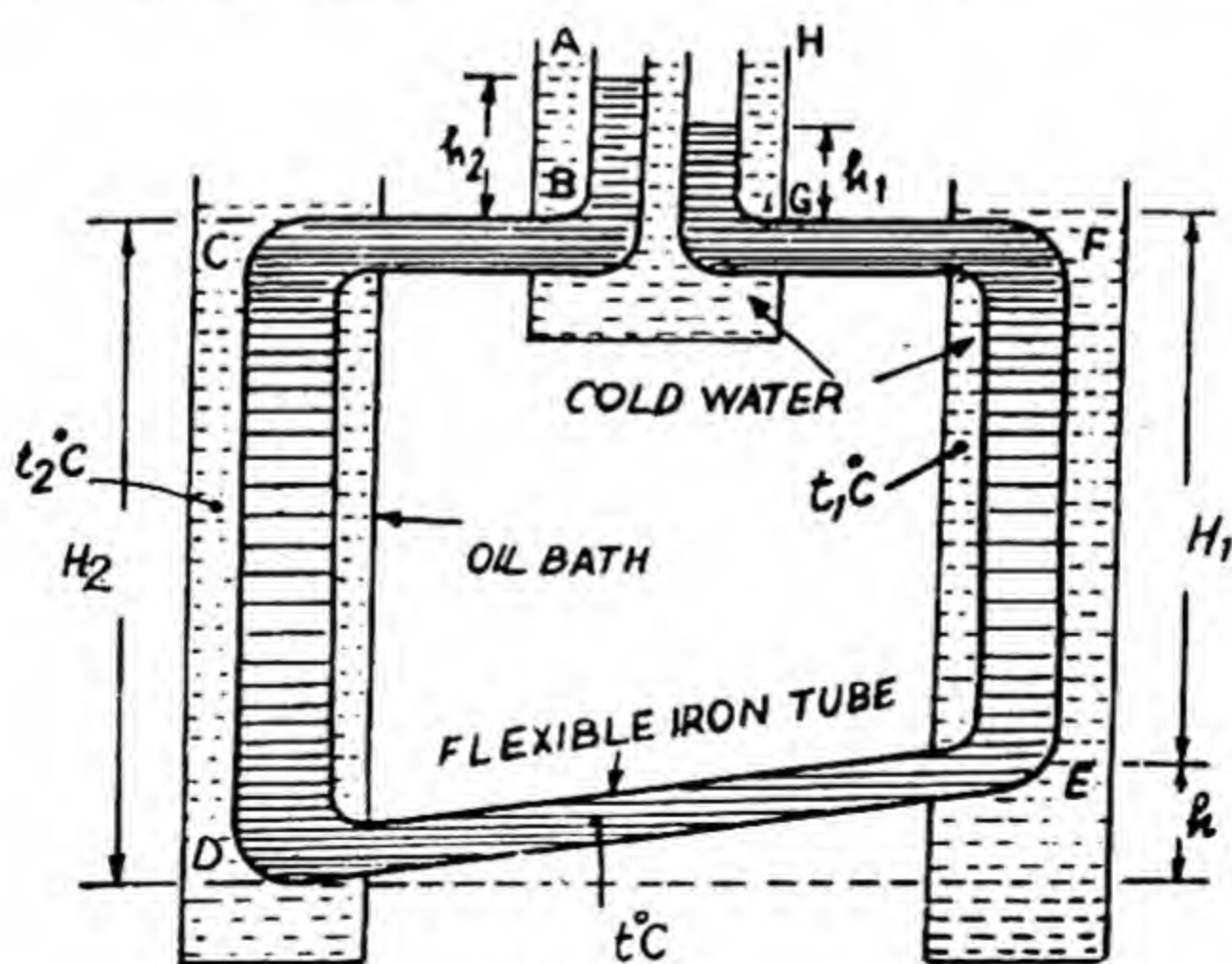


Fig. 2.8.

same level in part HG and AB . The vertical arm CD is

surrounded with an oil bath and the portions EF , AB and HG are jacketed with cold water baths fed from a common supply. The liquid in the tube CD expands. The level in AB , therefore, rises above the level in HG . When equilibrium is attained the various heights indicated on the diagram and their corresponding temperatures are measured. The portion DE is at room temperature $t^\circ C$. If ρ_1 , ρ_2 and ρ are the densities of the liquid at the temperatures t_1 , t_2 and $t^\circ C$ respectively.

Liquid pressure on the side $EFGH = h_1\rho_1 + H_1\rho_1 + h\rho$

Liquid pressure on the side $ABCD = h_2\rho_2 + H_2\rho_2$

In the equilibrium position, we have

$$h_2\rho_2 + H_2\rho_2 = h_1\rho_1 + H_1\rho_1 + h\rho$$

$$\text{But } \rho_0 = \rho_1(1 + \gamma_r t_1) = \rho_2(1 + \gamma_r t_2) = \rho(1 + \gamma_r t)$$

Where ρ_0 is the density of the liquid at $0^\circ C$ and γ_r is the coefficient of real or absolute expansion of the liquid.

Substituting these values of ρ_1 , ρ_2 and ρ in the above equation we have

$$\frac{h_2\rho_0}{(1 + \gamma_r t_2)} + \frac{H_2\rho_0}{(1 + \gamma_r t_2)} = \frac{h_1\rho_0}{(1 + \gamma_r t_1)} + \frac{H_1\rho_0}{(1 + \gamma_r t_1)} + \frac{h\rho_0}{(1 + \gamma_r t)}$$

$$\text{or } \frac{h_2}{(1 + \gamma_r t_2)} + \frac{H_2}{(1 + \gamma_r t_2)} = \frac{h_1}{(1 + \gamma_r t_1)} + \frac{H_1}{(1 + \gamma_r t_1)} + \frac{h}{(1 + \gamma_r t)}$$

All quantities except γ_r in this equation have been measured, so γ_r can be easily calculated.

Example 8. A U-tube contains mercury, its limbs being at $0^\circ C$ and $100^\circ C$ respectively. If the cold column is 60 cms. high and the hot column 1.8 cms. higher, what would be the coefficient of absolute expansion of mercury?

Height of the cold column $h_0 = 60$ cms.

Difference in the heights of the hot and cold column

$$h_t - h_0 = 1.80$$

Difference of temperature $t = 100 - 0 = 100^\circ C$

Let γ_r be the coefficient of absolute expansion of the liquid,

$$\therefore \gamma_r = \frac{h_t - h_0}{h_0 t} = \frac{1.8}{60 \times 100} = 0.003$$

Example 9. A column of mercury at $100^\circ C$ is balanced by a column at $0^\circ C$. The respective heights are 76.35 cms. and 75.00 cms. Calculate the coefficient of real expansion of mercury.

Height of mercury column at $0^\circ C = h_0 = 75$ cms.

Height of mercury column at $100^\circ C = h_{100} = 76.35$ cms.

Rise of temperature $t = 100^\circ C$

Now
$$\gamma_r = \frac{h_t - h_0}{h_0 \times t}$$

$$= \frac{76.35 - 75}{75 \times 100} = 0.00018$$

Example 10. The coefficient of linear expansion of glass is 3×10^{-6} and coefficient of cubical expansion of mercury is 1.8×10^{-4} . What volume of mercury must be placed in the specific gravity bottle in order that the volume of the bottle not occupied by mercury shall be the same at all temperatures ?

Let V_m and V_g be the volumes occupied by mercury and glass respectively at 0°C . Let $t^\circ\text{C}$ be the rise in temperature.

Increase in volume of the glass when temperature rises through

$$t^\circ\text{C} = V_g \times \gamma_g \times t$$

Increase in volume of the mercury when temperature rises through

$$t^\circ\text{C} = V_m \times \gamma_m \times t$$

The volume unoccupied by mercury will remain the same if the increase in volume of the vessel for a given rise in temperature is equal to the increase in volume of mercury for the same rise in temperature.

or
$$V_g \times \gamma_g \times t = V_m \times \gamma_m \times t$$

or
$$\frac{V_m}{V_g} = \frac{\gamma_g}{\gamma_m} = \frac{24 \times 10^{-6}}{1.8 \times 10^{-4}} = \frac{2}{15}$$

or
$$V_m = \frac{2}{15} V_g$$

i.e., volume occupied by mercury must be $\frac{2}{15}$ of the volume of the glass vessel.

Example 11. The coefficient of real expansion of mercury is 0.00018 and the coefficient of linear expansion of glass is 0.000009. Find what length of the tube of glass 300 mm. long must be filled with mercury in order that the volume unoccupied by mercury may remain the same at all temperatures.

Let l_m be the length of the tube occupied by mercury and $t^\circ\text{C}$ be the rise in temperature.

Increase in volume of mercury when temperature rises by $t^\circ\text{C}$

$$= V_m \times \gamma_m \times t = a l \gamma_r t$$

where a = area of cross-section of the tube, γ_m the coefficient of real expansion of mercury and γ_g the coefficient of cubical expansion of glass.

\therefore Increase in volume of the glass tube when the temperature rises by $t^\circ\text{C}$ $= V_g \gamma_g t = a l_g \gamma_g t = a \times 300 \times 3 \times 9 \times 10^{-6} \times t$

For the volume of the glass tube unoccupied by mercury to remain constant.

Increase in volume of mercury

= Increase in volume of the glass tube when the temperature rise by $t^{\circ}\text{C}$

$$\therefore al_m \gamma_{rt} = 300 a \gamma_{gl}$$

$$\text{or } l_m = 300 \frac{\gamma_g}{\gamma_m}$$

$$\therefore l_m = \frac{300 \times 27 \times 10^{-6}}{180 \times 10^{-6}} = \frac{300 \times 27}{180} = 45 \text{ mm.}$$

2.9. Anomalous expansion of water. Almost all liquids expand on being heated but water behaves in a peculiar manner. When water at 0°C is heated its volume decreases and

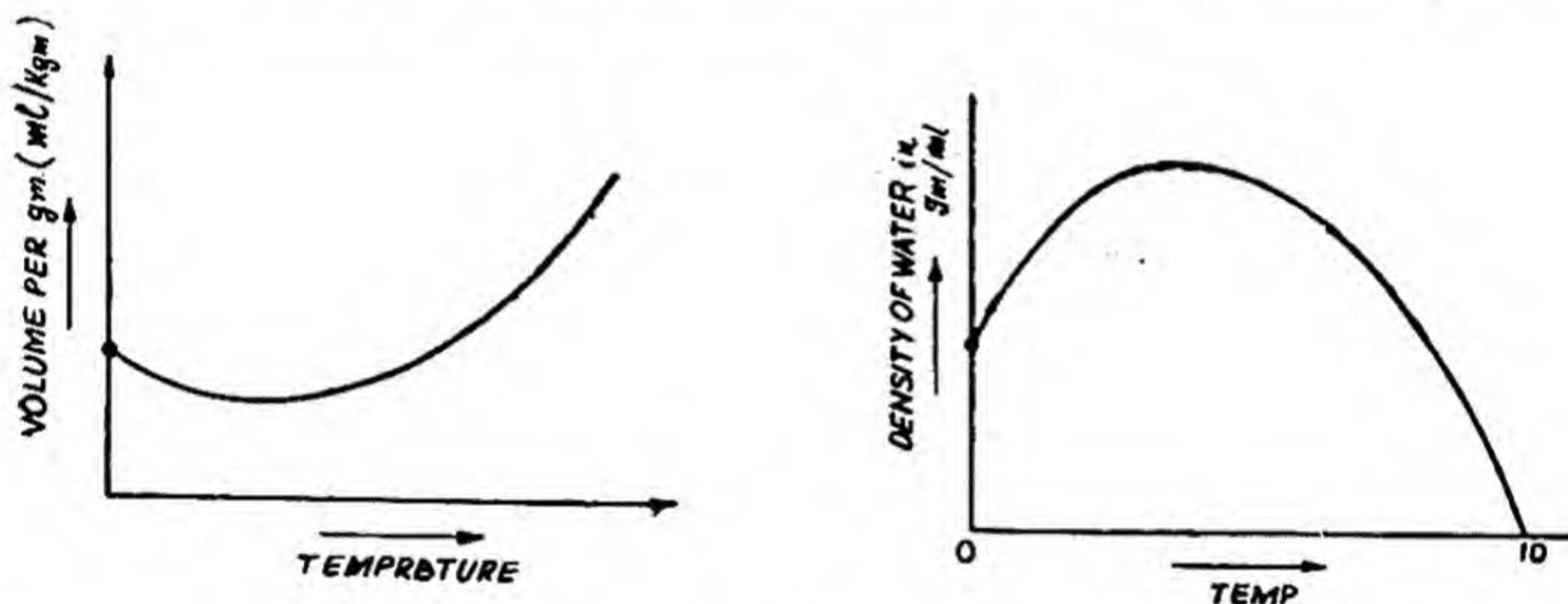


Fig. 2.9

therefore, its density increases upto a temperature of 4°C . After 4°C the rise in temperature causes an increase in volume and consequently a decrease in density. Water therefore, has a maximum density at 4°C . Variation of the density of water and volume of 1 gm. of water with temperature from 0°C to 10°C is shown in Fig. 2.9. In the graph between temperature and density, the density of water at 0°C is 0.99987 gm/ml , and at 10°C it is 0.99973 gm/ml .

[**Note.** The volume of water is minimum at 4°C or its density is maximum at 4°C and is equal to 1 gm/cm^3 . From the graph it is clear that from 4°C onwards, the graph between volume and temperature starts expanding though not uniformly. Its coefficient of expansion is different between different ranges of temperature].

The anomalous expansion of water makes it possible for fish and other aquatic animals to survive in winter time in countries where the temperature falls below 0°C and, ponds, lakes, rivers and seas freeze. Let us, for example, consider a lake where the air above, the water surface is below 0°C .

As the atmospheric temperature comes down the upper layers of water in lakes etc., cool and contract and sink to the bottom. This continues till the temperature of water in the lake reaches 4°C . When the top layers cool further, below 4°C the cold water being lighter does not go down but as further cooling takes place the top layer gradually freezes. Both water and ice are bad conductors of heat. The lower layers are, therefore, protected from freezing. Thus we see that water continues to exist at the bottom at 4°C though a thick layer of ice may have formed at the top. Thus marine life is saved from extinction by this anomalous expansion of water.

If water had contracted regularly like other liquids, the colder water would have settled at the bottom and ice formed at the bottom of the lake instead of at the top. During the short span of cold weather, the whole of the lake would have frozen that is would have become solid ice, thus perishing the entire marine life.

Example. 12. A piece of glass weighs 40 gms in vacuum and 28.0 gm. when immersed in water at 4°C and 28.486 gm. in water at its boiling point. If the coefficient of cubical expansion of glass is 27×10^{-4} per $^{\circ}\text{C}$, find the density of water at 100°C .

Mass of water displaced by glass piece at 4°C .

$$m_1 = w - w_1 = 40.5 - 28 = 12.5 \text{ gms.}$$

Mass of water displaced by glass piece at 100°C .

$$m_2 = w - w_2 = 40.5 - 28.486 = 12.014 \text{ gm.}$$

$$\text{Rise in temperature} = 100 - 4 = 96^{\circ}\text{C}$$

$$\therefore \gamma_a = \frac{m_1 - m_2}{m_2 \times t} = \frac{12.5 - 12.014}{12.014 \times 96} = 42.18 \times 10^{-6} \text{ per } ^{\circ}\text{C}$$

$$\begin{aligned} \text{But } \gamma_r &= \gamma_a + \gamma_g = 42.18 \times 10^{-6} + 27 \times 10^{-6} \\ &= 69.18 \times 10^{-6} \text{ per } ^{\circ}\text{C.} \end{aligned}$$

The specific volume of water is minimum at 4°C or its density is maximum at 4°C and is equal to 1 gm/cm^3

$$\therefore \rho_4 = 1 \text{ gm/cm}^3$$

$$\text{But } \rho_4 = \rho_{100} (1 + \gamma_r t) = \rho_{100} (1 + 69.18 \times 10^{-6} \times 96)$$

$$\therefore 1 = \rho_{100} (1 + 69.18 \times 10^{-6} \times 96)$$

$$\begin{aligned} \text{or } \rho_{100} &= \frac{1}{(1 + 69.18 \times 10^{-6} \times 96)} \\ &= (1 - 69.18 \times 10^{-6} \times 96) = 1 - 0.0662 = 0.9338 \text{ gm/cm}^3 \end{aligned}$$

Expected Questions

1. (a) Define coefficient of cubical expansion. What is the distinction between real and apparent expansion in the case of a liquid?

(b) Explain the terms absolute expansion and apparent expansion and how they are related. (A.M.I.E.)

2. Explain proving any formula involved, how a dilatometer is used for measuring the coefficients of expansion of a liquid.

3. Describe with relevant theory, Regnault's methods of determining the absolute co-efficient of expansion. (A. M. I. E.)

4. You are provided with a solid of known coefficient of expansion and which sinks in the liquid. Describe giving relevant theory, how you would determine the real coefficient of expansion of the liquid.

5. Write a note on the anomalous expansion of water. (A. M. I. E.)

6. Water is not at all suitable as thermometric liquid between 0°C and 8°C but a particular property of water saves the lives of the aquatic animals in very cold countries.

Explain this statement as clearly as possible.

(Aero Society of Engineers)



CHAPTER III

EXPANSION OF GASES

3.1. Introduction. Mechanical engineers who design engines of all types must know how the gases inside them expand and contract when they are subjected to changes of temperature and pressure. On this account the subject of "The Expansion of Gases" has considerable practical importance.

Gases like solids and liquids change in volume with change in temperature and they do so at a much higher rate. Moreover, while discussing the expansion of solids the effect of pressure was not taken into consideration because the change in volume of a solid or a liquid with pressure is almost negligible. But in the case of gases, the change in pressure, considerably affects the volume even when the temperature is kept constant. Thus in the case of a gas, we must take into account three variables—the volume (V), the temperature (T) and the pressure (P).

These variables are related to and mutually depend upon one another and in order to study the relation between any two, the third must be kept constant. We can have the following three relationships ;

(i) the relation between pressure and volume at constant temperature (Boyle's Law).

(ii) the relation between volume and temperature at constant pressure (Charle's Law).

(iii) the relation between pressure and temperature at constant volume (Law of pressures or Gay Lussac's Law).

These laws are known as **Gas Laws**.

3.2. Boyle's Law. Robert Boyle in 1662 discovered that at constant temperature the volume of a given mass of a gas is inversely proportional to the pressure.

$$\text{Mathematically } P \propto \frac{1}{V}$$

or

$$PV = a \text{ constant} = K$$

The constant K depends upon the mass, nature and the temperature of the gas. The equation $PV = \text{constant}$ is called the isothermal equation of the state of a gas. If the pressure and volume of a gas change from P_1, V_1 to P_2, V_2 at constant temperature, then the equation is

$$P_1V_1 = P_2V_2 = \dots = K$$

If a curve is drawn for P and V taking V along the abscissa and P along the ordinate, then the curve will be a rectangular hyperbola as shown in the Fig. 3.1.

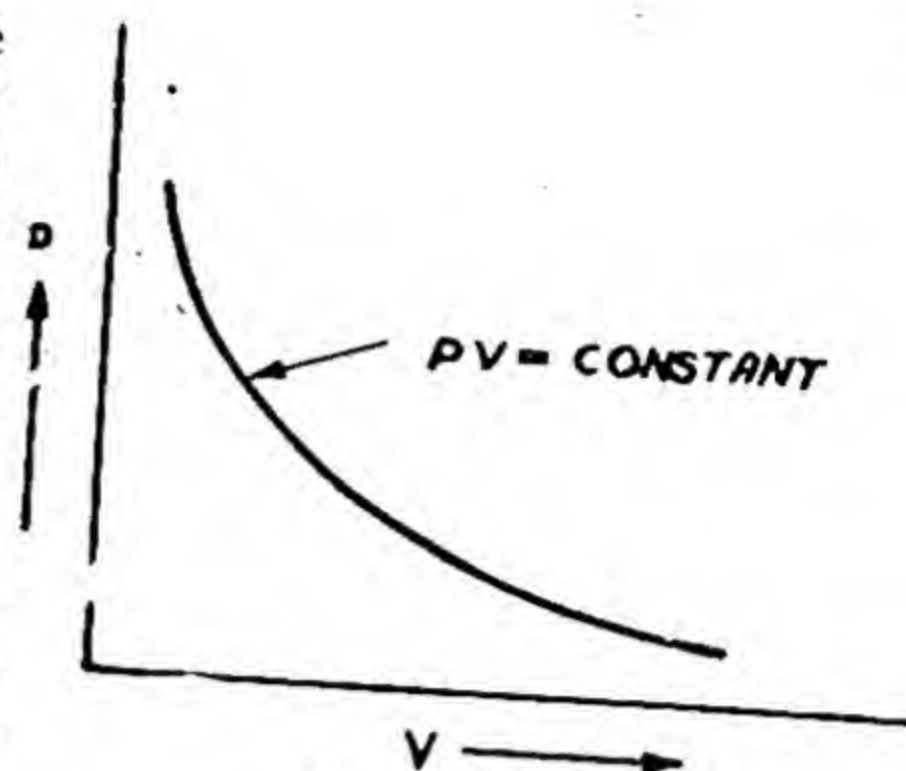


Fig. 3.1.

Limitations of Boyle's Law. Boyle verified this law for a small range of pressures. Despretz showed that the volumes of carbon dioxide and ammonia decreased more rapidly with increase of pressure than would be expected from Boyle's law. Hence this law does not hold good rigorously at high pressures.

Further investigations showed that it is true for any gas remote from its point of liquefaction. Hence this law is correct for the permanent gases such as hydrogen, oxygen, nitrogen etc., at temperatures remote from their temperatures of liquefaction.

Example. 1. What is the pressure inside a motor cycle tyre if its internal volume is 150 litres and 260 litres of air at atmospheric pressure is used to fill it up by a pump?

According to Boyle's law

$$P_1V_1 = P_2V_2$$

or $1 \times 260 = P_2 \times 150$

$$\therefore P_2 = \frac{260}{150}$$

$$= 1.733 \text{ atmospheres}$$

Example. 2. In a simple barometer tube standing in mercury the length of the mercury column is 74 cms. when the tube is depressed so that the volume of the space above mercury level is halved, the length of the mercury column is only 72 cms. Find the atmospheric pressure,

If there is a perfect vacuum in the space above mercury, no change in the length of the mercury column should take place when the tube is depressed. As the volume is changing on depressing the tube, some air is present above the mercury column.

Let P be the atmospheric pressure and P_1 and P_2 the pressures exerted by the air present above mercury in the two cases.

Apparent atmospheric pressure in case I = 74.0 cm of Hg.

$$\therefore P = 74 + P_1 \text{ or } P_1 = (P - 74)$$

Apparent atmospheric pressure in case II = 72 cm of Hg.

$$\therefore P = 72 + P_2 \text{ or } P_2 = (P - 72)$$

Let V_1 and V_2 be the volumes of the air present in the space above mercury in the two cases respectively, then

$$V_2 = \frac{1}{2} V_1$$

According to Boyle's Law,

$$P_1 V_1 = P_2 V_2$$

$$(P - 74) V_1 = (P - 72) V_2$$

$$\text{or } (P - 74) V_1 = (P - 72) V_1 / 2$$

$$\text{or } 2P - 148 = P - 72$$

$$\begin{aligned} \text{or } P &= 148 - 72 \\ &= 76.0 \text{ cms of Hg.} \end{aligned}$$

Example. 3. The volume of Torricellian Vacuum is 6 cm^3 and its length 12 cm. If 7 cm^3 of air at the pressure of the atmosphere, which is 76 cm. are introduced into the barometer tube, by how much will the the mercury column be depressed?

The volume of air at atmospheric pressure before being introduced in the barometer tube $V_1 = 7 \text{ cm}^3$.

Height of mercury column = Atmospheric pressure. $P_1 = 76 \text{ cm.}$

Let this air depress the mercury column by $x \text{ cm.}$

$$\therefore \text{Increase in volume of air} = x \times \frac{6}{12} = 0.5 x$$

$$\text{The volume of air in the tube } V_2 = (6 + 0.5x) \text{ cm}^3$$

$$\text{Pressure of air } P_2 = x \text{ cm of mercury.}$$

By Boyle's Law, we have

$$P_1 V_1 = P_2 V_2$$

$$\therefore 76 \times 7 = x \times (6 + 0.5 x)$$

$$532 = 6x + 0.5x^2$$

$$\text{or } x^2 + 12x - 1064 = 0$$

$$\begin{aligned} \therefore x &= \frac{6 \pm \sqrt{(6)^2 + 4 \times 1064}}{2 \times 6} \\ &= \frac{6 \pm \sqrt{492}}{12} = \frac{6 \pm 65.5}{12} = 5.96 \text{ cm.} \end{aligned}$$

Example. 4. A little air has leaked into a barometer tube one metre long. The mercury stands at 75 cms mark, when the tube is vertical and at 83 cm. mark when the tube is inclined at 30° to the vertical. What is atmospheric pressure?

Let the true atmospheric pressure be P cm. of mercury column.

(i) When the tube is vertical.

Pressure of air inside the tube

$P_1 = (P - 75)$ cm. of mercury
and volume of air $V_1 = (100 - 75) a = 25 a$ cm³
where a = area of cross-section of the tube.

(ii) When the tube is inclined

Vertical height of mercury column $= 83 \times \cos 30^\circ$
 $= 83 \times 0.866$
 $= 71.9$ cm.

Pressure of air inside the tube

$P_2 = (P - 71.9)$ cm. of mercury

and volume of air $V_2 = (100 - 83) a = 17a$ cm³

By Boyle's Law, we have

$$P_1 V_1 = P_2 V_2$$

$$(P - 75) \times 25a = (P - 71.9) \times 17a$$

$$(P - 75) \times 25 = (P - 71.9) 17$$

$$25P - 1875 = 17P - 1222.3$$

$$8P = 1875 - 1222.3 = 652.7$$

or

$$P = \frac{652.7}{8}$$

$$= 81.6 \text{ cm. of Hg}$$

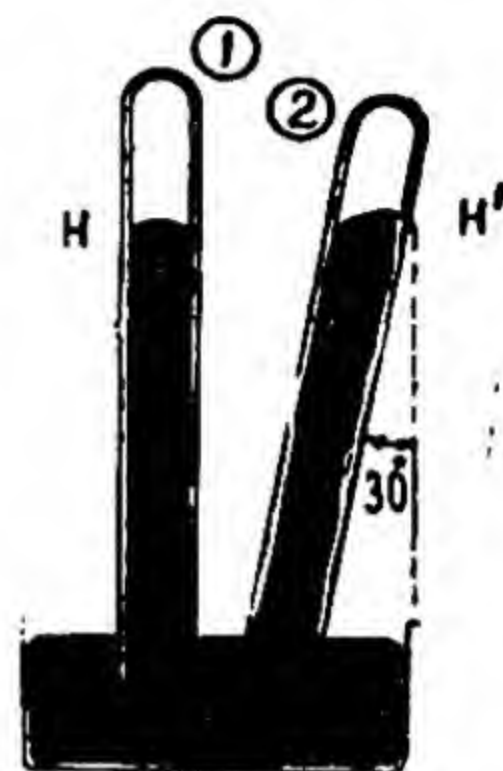


Fig. 3.1.

3.3. Charles's Law. The relation between volume and temperature of a gas at constant pressure is given by Charles's Law. It states that *Pressure remaining constant, the volume of a given mass of any gas increases (or decreases) by the constant fraction $\frac{1}{273}$ of its volume at 0°C for each degree centigrade rise (or fall) in temperature,*

The fraction $\frac{1}{273}$ (0.00367) is the coefficient of increase of volume at constant pressure for all gases. It is denoted by γ_p and is defined as the increase in volume per unit volume of a gas at 0°C for 1°C rise in temperature, provided the pressure remains constant.

If V_0 and V_t are the volumes of a given mass of a gas at 0°C , and $t^\circ\text{C}$ respectively, then according to Charles's Law, we have

$$V_t = V_0 (1 + \gamma_p t)$$

$$\gamma_p = \frac{V_t - V_0}{V_0 t}$$

(i)

The value of γ_p depends upon the scale of temperature used.

$$\gamma_p = \frac{1}{273} (0.00367) \text{ per } ^\circ\text{C}$$

and $\gamma_p = \frac{1}{460} \text{ or } (0.00217) \text{ per } ^\circ\text{F}$

The equation (i) can be written as

$$V_t = V_0 \left(1 + \frac{t}{273} \right) \text{ when } t \text{ is in } ^\circ\text{C}$$

$$V_t = V_0 \left(1 + \frac{t}{460} \right) \text{ when } t \text{ is in } ^\circ\text{F}$$

Example. 5. In an experiment for finding the coefficient of expansion of air at constant pressure the volume of air at 30°C was 75 c.c. When the air was heated to 98°C , keeping the pressure constant, it occupied 92 c.c. Calculate the coefficient of expansion of air.

Let V_1 be the volume of air at 30°C and V_2 at 98°C .

Let γ_p be the coeff. of expansion of air when pressure is kept constant.

Hence applying the formula.

$$\text{Now } V_t = V_0 (1 + \gamma_p t)$$

where γ_p is the co-efficient of expansion of air at constant pressure

$$\therefore V_1 = V_0 (1 + \gamma_p 30) \quad \dots (i)$$

$$\text{and } V_2 = V_0 (1 + \gamma_p 98) \quad \dots (ii)$$

Dividing (ii) by (i) we have

$$\frac{1 + 98\gamma_p}{1 + 30\gamma_p} = \frac{92}{75}$$

$$\text{or } \gamma_p = 0.00426$$

3.4. Gay Lussac's Law. When a given mass of gas is heated, keeping its volume constant, its pressure increases. This is because the gas on heating tends to expand. But it is not allowed to do so, as the volume is kept constant. This, therefore, results in an increase of pressure. There is a definite relation between the temperature and the pressure of a gas at constant volume and this relation is known as the Law of pressures or constant volume law. It states that.

The volume remaining constant, the pressure of a given mass of a gas increases (or decreases) by $\frac{1}{273}$ of its pressure at 0°C , for each degree centigrade rise (or fall) in temperature.

This law is sometimes called as **Second Charles's law of pressure.**

Thus if P_0 and P_t are the pressures of a gas at 0°C and $t^\circ\text{C}$ respectively at constant volume, we have.

$$P_t = P_0 (1 + \gamma_v t)$$

$$\text{or } \gamma_v = \frac{P_t - P_0}{P_0 t}$$

where γ_v is the coefficient of increase of pressure at constant volume (or simply pressure coefficient) and its value is $\frac{1}{273}$ or 0.00367. The pressure coefficient (γ_v) is defined as the increase in pressure per unit pressure at 0°C per $^\circ\text{C}$ rise of temperature.

The value of γ_v depends up on the scale of temperature used. Thus

$$\gamma_v = \frac{1}{273} \text{ or } (0.00367) \text{ per } ^\circ\text{C}$$

$$\text{and } \gamma_v = \frac{1}{460} \text{ or } (0.00217) \text{ per } ^\circ\text{F}$$

Again relation (i) can be written as

$$P_t = P_0 \left(1 + \frac{t}{273} \right) \text{ if } t \text{ is in } ^\circ\text{C}$$

If the temperature t is measured in $^\circ\text{F}$, then

$$P_t = P_0 \left(1 + \frac{t}{460} \right)$$

3.5. Absolute Temperature. If a given mass of a gas is slowly cooled at constant pressure, its volume decreases uniformly with the temperature. As the gas is below 0°C its volume shrinks further and theoretically, there is a definite temperature at which the volume of the gas would become zero. The temperature at which the volume of the gas becomes zero is called the **absolute zero** and represents the lowest temperature that can be conceived, or attained.

Consider the relation $V_t = V_0 \left(1 + \frac{t}{273} \right)$

If $V_t = 0$, then

$$0 = V_0 \left(1 + \frac{t}{273} \right)$$

or $t = -273$

Thus the absolute zero is -273°C . In other words 0°C is 273 degrees above the absolute zero, 100°C is 373 degrees above the absolute zero. Actually all the gases liquify before the absolute temperature is reached. When temperatures are measured from the absolute zero they are said to be **absolute temperatures** and are expressed in "degrees Kelvin" ($^\circ\text{K}$) or degrees Absolute ($^\circ\text{A}$). The scale of temperature having its zero at the absolute zero is called the absolute scale or Kelvin's scale. The absolute temperature corresponding to $t^\circ\text{C}$ is given by

$$T^\circ\text{K or } T^\circ\text{A} = (273 + t)$$

Thus $0^{\circ}\text{C} = 273^{\circ}\text{K} = 273^{\circ}\text{A}$

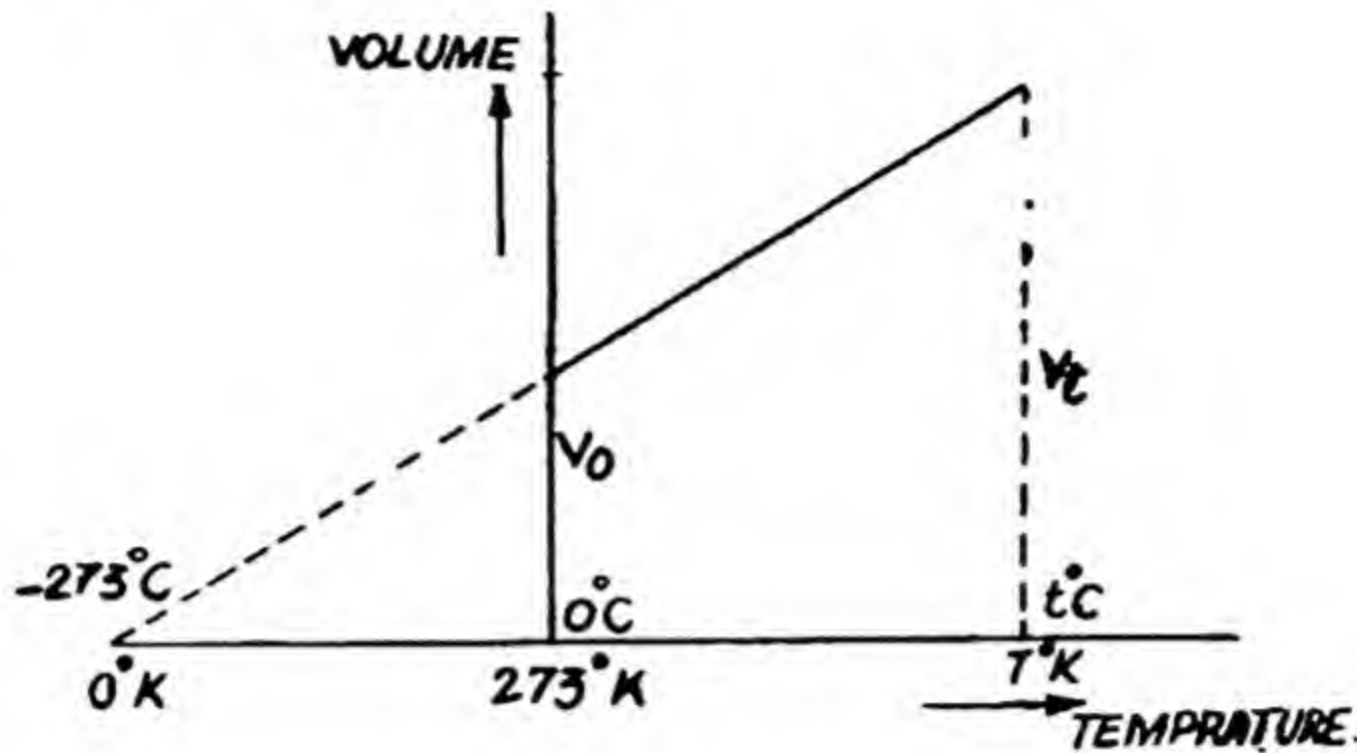


Fig. 3.2.

The value of absolute zero on Fahrenheit scale is -460°F .

Hence the absolute temperature corresponding to $t^{\circ}\text{F}$ is given by

$$T^{\circ}\text{R} = (460 + t)$$

where R denotes Rankin's scale corresponding to absolute zero of -460°F .

3.6. Alternative Form of Charles's Law. *It states that the volume of a given mass of a gas is proportional to its absolute temperature at constant pressure.*

If V_1 and V_2 be the volumes of a given mass of a gas at $t_1^{\circ}\text{C}$ and $t_2^{\circ}\text{C}$ respectively at constant pressure, then

$$\begin{aligned} V_1 &= V_0 \left(1 + \frac{t_1}{273} \right) \\ &= V_0 \left(\frac{273 + t_1}{273} \right) = V_0 \frac{T_1}{T_0} \end{aligned}$$

where V_0 = volume of the gas at 0°C
 $T_1^{\circ}\text{K} = (273 + t_1^{\circ}\text{C})$

and

$$T_0^{\circ}\text{K} = (273 + 0^{\circ}\text{C})$$

\therefore

$$V_1 = V_0 \frac{T_1}{T_0}$$

or

$$\frac{V_1}{V_0} = \frac{T_1}{T_0}$$

(i)

Similarly

$$\frac{V_2}{V_0} = \frac{T_2}{T_0}$$

(ii)

From (i) and (ii), we have

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} = \text{a constant}$$

or
$$\frac{V}{T} = \text{a constant}$$

Hence
$$V \propto T$$

In other words the volume of a given mass of a gas is proportional to the absolute temperature, when pressure remains constant

Example. 6. *A gas at 13°C has its temperature raised so that its volume is doubled, the pressure remaining constant. What is its final temperature.*

Let $t^{\circ}\text{C}$ be the temperature to which the gas has been heated so that its volume is doubled.

Initial temperature $T_1 = 273 + 13 = 286^{\circ}\text{A}$

Initial volume $= V_1$

Final volume $= 2V_1$

Final temperature $T_2 = (t + 273)^{\circ}\text{A}$

As pressure remains constant, so according to Charle's Law.

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or
$$T_2 = \frac{V_2}{V_1} \times T_1$$

$$273 + t = \frac{2V_1}{V_1} \times 286$$

or
$$273 + t = 572$$

or
$$t = 572 - 273$$

$$= 299^{\circ}\text{C}$$

Example. 7. *The density of Argon is 1.6 gm/litre at 26°C and at a pressure of 76 cm of mercury. What is the mass of Argon in the gas filled lamp bulb of volume 100 c. c. , the pressure inside is 76 cm. of mercury when the average temperature of the gas is 120°C ?*

Let volume of Argon at $120^{\circ}\text{C} = (273 + 120)^{\circ}\text{K}$ and at a pressure of 76 cm of Hg, $V_1 = 100 \text{ c. c.}$

and the volume at temperature 26°C , $(273 + 26)^{\circ}\text{K}$, at the same pressure $= V_2$

According to Charle's law as the pressure remains constant

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

or
$$V_2 = V_1 \times \frac{T_2}{T_1} = 100 \times \frac{299}{393}$$

$$\therefore V_2 = 76 \text{ cm}^3.$$

Since the density of Argon at $26^\circ\text{C} = 1.5 \text{ gm/litre}$

$$\therefore \text{mass of 1 litre (1000 cm}^3\text{) of Argon at } 26^\circ\text{C} = 1.5 \text{ gm.}$$

and mass of 76 cm^3 of Argon gas at 26°C

$$= \frac{1.5}{1000} \times 76 = 0.114 \text{ gm.}$$

3.7. Alternative Form of Pressure Law or Gay Lussac's Law. *It states that at constant volume the pressure exerted by a given mass of a gas is proportional to its absolute temperature.*

Let P_0 and P_t be the pressures of a given mass of a gas at 0°C and $t^\circ\text{C}$ respectively at constant volume, then

$$P_t = P_0 \left(1 + \frac{t}{273} \right)$$

$$\text{or } P_t = P_0 \left(\frac{273 + t}{273} \right)$$

$$= P_0 \frac{T}{T_0}$$

$$\text{or } \frac{P_t}{T} = \frac{P_0}{T_0}$$

where T and T_0 are the absolute temperatures corresponding to $t^\circ\text{C}$ and 0°C respectively.

In other words at constant volume, the pressure of a given mass of gas is proportional to the absolute temperature.

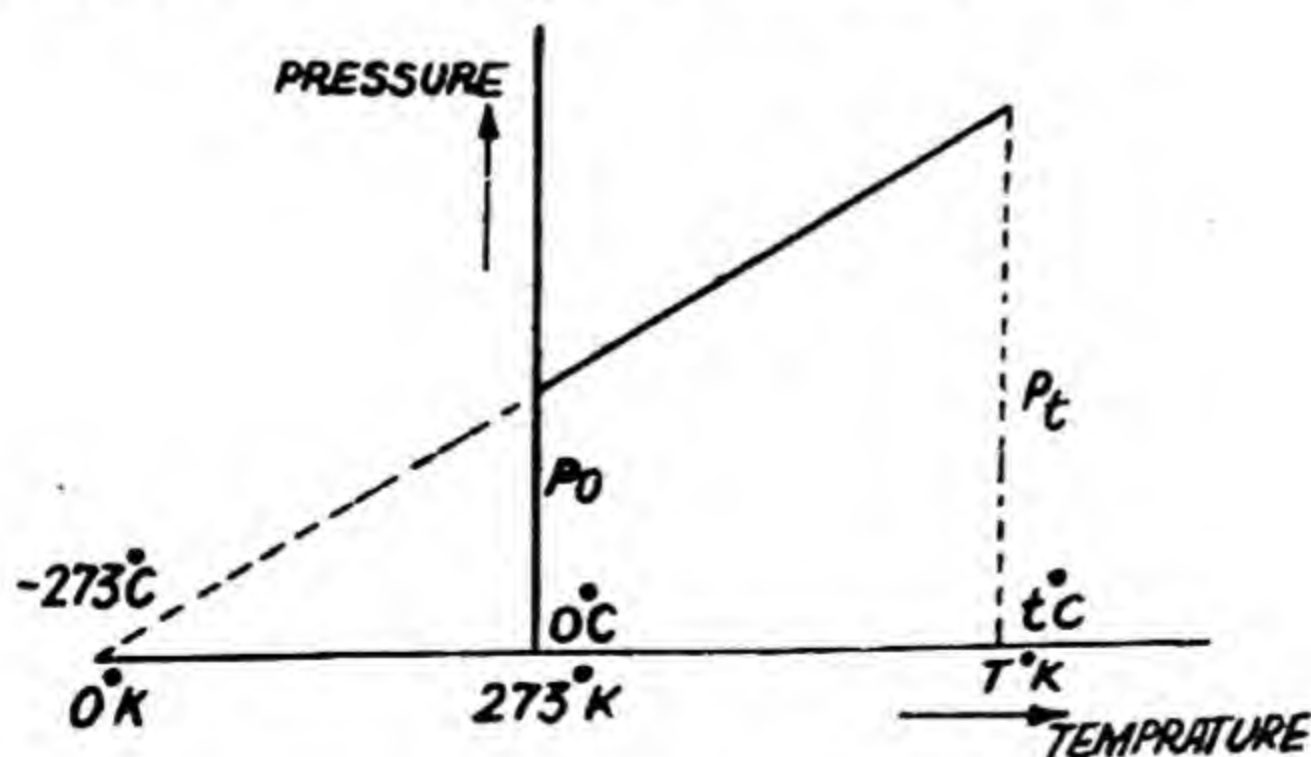


Fig. 3.3.

If P_1 and P_2 are the pressures of a gas at absolute temperatures T_1 and T_2 respectively, then

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

and

$$\frac{P_2}{T_2} = \frac{P_0}{T_0}$$

or

$$\frac{P_2}{T_2} = \frac{P_1}{T_1}$$

3.8. Relation between γ_v and γ_p . We have already stated that experiment shows that the volume coefficient γ_v of a perfect gas is $\frac{1}{273}$, the same value as for the pressure coefficients γ_p for a perfect

gas. The equality of γ_p and γ_v can also be shown to follow if the gas obeys **Boyle's Law** and **Charles's Law**.

Let a given mass of a gas having a volume V_0 and pressure P_0 at 0°C be heated twice from 0°C to $t^\circ\text{C}$ firstly at constant volume (V_0)

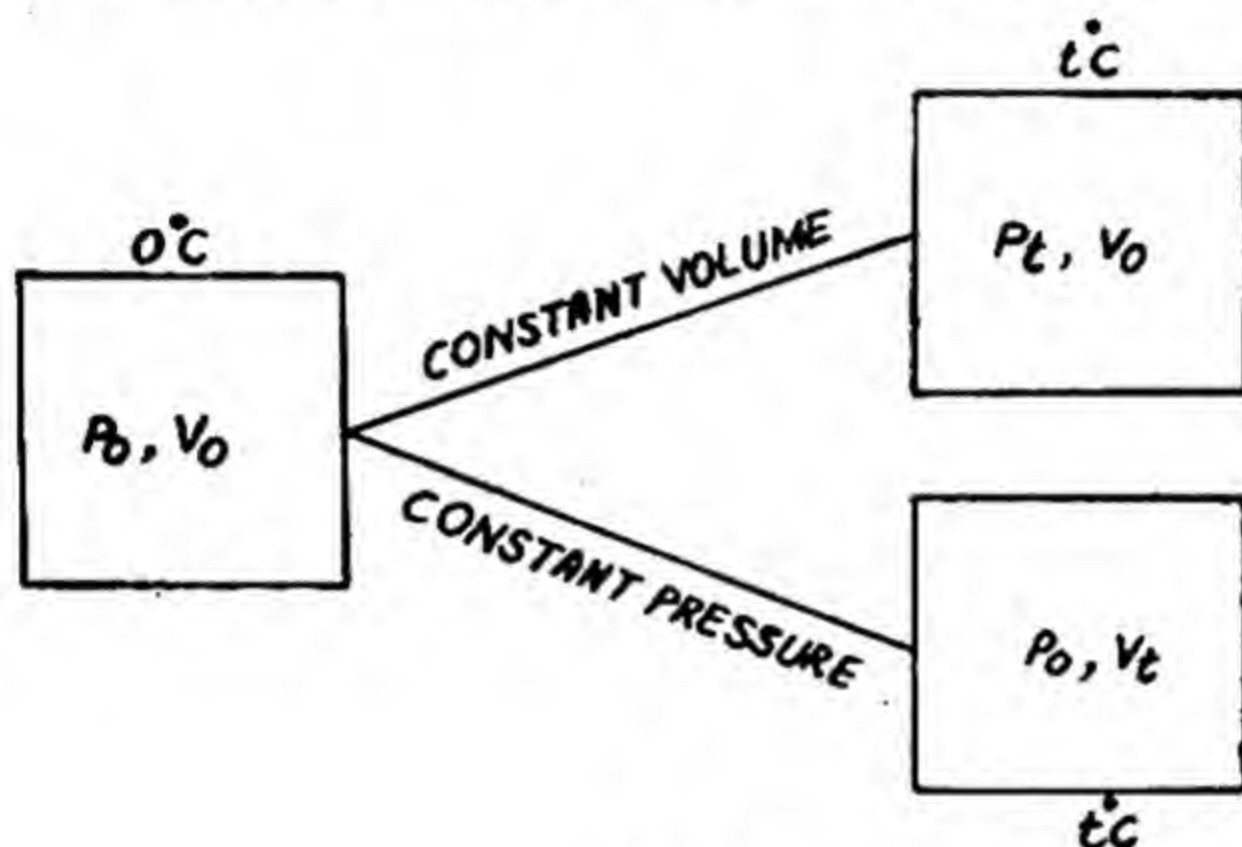


Fig 3.4.

when the pressure changes from P_0 to P_t and secondly at constant pressure (P_0) when the volume changes from V_0 to V_t . Since the temperature $t^\circ\text{C}$ is the same in either case, it follows from Boyle's Law that

$$P_0 V_t = P_t V_0$$

$$\therefore \frac{P_t}{P_0} = \frac{V_t}{V_0} \quad \dots(1)$$

But $V_t = V_0 \left(1 + \frac{t}{273} \right)$ assuming Charles's Law

$$\therefore \frac{V_t}{V_0} = 1 + \frac{t}{273}$$

Substituting the value of $\frac{V_t}{V_0} = 1 + \frac{t}{273}$ in (1), we have

$$\frac{P_t}{P_0} = 1 + \frac{t}{273}$$

Thus
$$P_t = P_0 \left(1 + \frac{t}{273} \right)$$

It follows from the above relation that the pressure coefficient γ_p is also $\frac{1}{273}$.

Thus the volume coefficient of the gas is equal to its pressure coefficient if it obeys Boyle's and Charle's Law.

3.9. Ideal gas. An ideal gas or **perfect gas** is one which strictly obeys the gas laws. There is, however, no gas which perfectly obeys all the gas laws. Some gases like hydrogen, nitrogen, oxygen, helium etc., the so called permanent gases, obey the gas laws with sufficient accuracy. These gases therefore, are considered to be perfect for all practical purposes.

Example. 8. A given volume of air has 740 mm. pressure at 17°C . What is the temperature in centigrade scale when its pressure is 1850 mm.

Initial pressure of air $P_1 = 740 \text{ mm.} = 74.0 \text{ cm.}$

Initial temperature of air $T_1 = 273 + 17 = 290^\circ\text{A.}$

Final pressure of air $P_2 = 1850 \text{ mm.} = 185.0 \text{ cm.}$

Let $t^\circ\text{C}$ be the final temperature of the air, then

Final temperature of air $T_2 = (273 + t)^\circ\text{A.}$

Applying Gay Lussac's Law, we have

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

or
$$T_2 = \frac{P_2}{P_1} \times T_1$$

$$\frac{185.0}{74.0} \times 290 = 725^\circ\text{A}$$

But
$$T = 273 + t$$

$\therefore 273 + t = 725$

or
$$t = 452^\circ\text{C}$$

Example. 9. The volume of a gas at N.T.P. is 250 c.c. Its temperature is increased to 55°C and the pressure by 145 mm., the volume remaining constant. Find the pressure coefficient of the gas with temperature.

Let $P_1 = 76.0 \text{ cm.}$ be the normal pressure at 0°C or 273°A and P_2 the pressure at 55°C .

$$P_2 = 76 + 14.5 = 90.5 \text{ cm.}$$

and
$$T_2 = 55^\circ\text{C} = 273 + 55 = 325^\circ\text{A.}$$

Now
$$P_t = P_0(1 + \gamma_v t)$$

$\therefore \gamma_v = \frac{90.5 - 76.0}{76 \times 55} = \frac{14.5}{76 \times 55} = 0.00348$

Example. 10. It is found that the volume of a certain gas increases in the ratio 1.035 : 1 between 25°C and 15°C . Calculate the absolute zero on the centigrade scale for this gas.

Suppose the absolute zero is $x^{\circ}\text{C}$. Then assuming that the change of volume takes place at constant pressure, we have

$$\frac{V_2}{V_1} = \frac{T_2}{T_1} \text{ where } T_2 \text{ and } T_1 \text{ are the absolute temperatures}$$

for this gas.

$$\therefore \frac{1.035}{1} = \frac{x+25}{x+15}$$

$$\therefore x = -270.7^{\circ}\text{C}$$

3.10. Gas Equation. The gas laws, discussed in the preceding articles give relations between two variables of a gas when the third variable is kept constant. If, however, all the three variables P , V and T , change simultaneously, then the relationship between them is given by an equation known as **Gas Equation** which is a combination of Boyle's and Charle's Laws.

Let V_1 be the volume of a given mass of a gas at a pressure P_1 and temperature $T_1^{\circ}\text{A}$. If the pressure changes to P_2 and temperature to T_2 , the new volume V_2 can be calculated as follows.

Suppose the whole process takes place in two steps. In the first step the pressure changes to P_2 but the temperature remains constant. In such a case Boyle's law is applicable. If, therefore the new volume is v , then

$$P_1V_1 = P_2v = \text{constant} \quad (1)$$

In the second step suppose the pressure remains constant at P_2 but the temperature changes from T_1 to T_2 . If V_2 be the final volume then, according to Charles' law.

$$\frac{V_2}{v} = \frac{T_2}{T_1} = \text{constant} \quad (2)$$

Hence substituting the value of v from (1) in (2), we get

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} = \text{a constant (say } K)$$

This is called the gas equation and in general is written as

$$\frac{PV}{T} = \text{a constant}$$

Thus the product of the pressure P and the volume V of a given mass of a gas varies directly as its absolute temperature T . The relation as given above is also known as equation of state for a gas because when the values of any two out of the three quantities P , V and T are known, the third quantity can easily be found out. The value of constant K depends upon the mass and properties of the gas concerned.

If V is the gram molecular volume, then constant K is taken as R and is known as gram molecular gas constant or universal gas constant. Its value is the same for all gases because one gram molecule of all gases at $N.T.P.$ or $S.T.P.$ (normal temperature $273^{\circ}A$ and pressure 760 mm) has the same volume.

The equation then becomes

$$PV = RT$$

This equation is known as characteristic gas equation.

In the C.G.S. system R is measured in erg/gm per $^{\circ}A$ or cal/gm per $^{\circ}A$.

In the M.K.S. system R is measured in Joules/kg. per $^{\circ}A$ or Kilo cal/kg per $^{\circ}A$

In the F. P. S. system R is measured in ft. lbs/lb per $^{\circ}R$ or B.Th. U/lb per $^{\circ}R$.

If we choose to deal with 1 gm. of a given gas, then the constant K in equation is usually written as r and is called as the "**Characteristic Gas Constant**" or simply the **Gas constant**.

Thus $PV = rT$ for unit mass of a gas and this equation is known as the *characteristic equation of a perfect gas*.

The value of r depends upon the nature of gas and hence its value varies from gas to gas. The value of r for any gas can be calculated from the above equation if the volume of the gas at $N.T.P.$ or $S.T.P.$ is known. The units of r in different system of units are the same as those of R .

The gas constant r for oxygen can be calculated from the observations that the volume of 1 gm of the gas at $N.T.P.$ is 700 c.c., the pressure P of the gas is 76 cm. of mercury and the temperature of the gas is $0^{\circ}C$ so that its absolute temperature T is $273^{\circ}A$.

Hence

$$r = \frac{PV}{T} = \frac{h\rho g \times V}{T}$$

$$\therefore r = \frac{(76 \times 13.6 \times 980) \times 700}{273}$$

$$= 2.6 \times 10^6 \text{ ergs/gm/degree } A$$

Note (i) $P = h\rho g$ where h is the height of the mercury column in cm.

V = Volume in c.c.

T = Temperature in degrees absolute

(ii) ρ is the density of mercury.

(iii) g is the acceleration due to gravity in cms/sec².

The value of r in the case of hydrogen can be calculated as under.

1 gm of hydrogen occupies a volume of 11.2 litres at $N.T.P.$ so that $V = 11.2 \times 1000$ c.c., pressure $P = 76$ cm. and Temperature $T = 273^{\circ}A$.

$$\therefore r = \frac{PV}{T} = \frac{76 \times 13.6 \times 980 \times 11200}{273} = 4.15 \times 10^7 \text{ ergs/gm/}^{\circ}A.$$

Example. 11. 1 Kg. of air at *N.T.P.* occupies 0.7734 cubic metre. Calculate the value of the gas constant for the gas.

In *M.K.S.* system of units the pressure P is measured in Newtons/metre²

$$\therefore P \text{ in Newtons/m}^2 = \frac{h\rho g}{10^5} \times 10^4$$

$$= \frac{h\rho g}{10} = \frac{76 \times 13.6 \times 981}{10} = 1.014 \times 10^5 \text{ Newtons/m}^2.$$

Applying the equation $r = \frac{PV}{T}$

we have

$$r = \frac{1.014 \times 10^5 \times 0.7734}{273} = 287 \text{ joules/Kg/}^\circ A.$$

3.11. General gas equation. We have seen that gas equation holds good for unit mass of a gas. If now m gm. of the gas having a volume V is considered, then the gas equation becomes

$$PV = mrT$$

or
$$m = \frac{PV}{rT}$$

This equation can be used to find the mass of certain a volume of the gas, provided the gas constant r for one gm. is known. Further, once the mass is calculated, the density ρ of the gas can easily be

determined from the relation $\rho = \frac{m}{V}$.

3.12. Universal gas Constant. If a gramme molecule of a gas is taken the value of the constant K in the gas equation is denoted by R and is known as gram-molecular gas constant or universal gas constant. Its value is the same for all gases because one gramme molecule of all gases at *N.T.P.* has the same volume of 22.4 litres.

The gram molecular gas equation is $PV = RT$

The gas equation can also be expressed by $PV = MrT$ where M is the gram-molecular weight and r is the gas constant for one gram.

Hence $M \times r = R$ i.e. $M = \frac{R}{r}$

$$\therefore \text{Molecular weight of a gas} = \frac{\text{Universal gas constant}}{\text{characteristic gas constant}}$$

Numerical Value of the Universal gas Constant.

The universal gas constant is given by the relation

$$R = \frac{PV}{T}$$

Normal pressure = 76 cm of mercury column

Temperature = $273^\circ A$.

Volume of one gm mol of gas = 22.4 litres = 22400 c.c.

$$\therefore R = \frac{76 \times 13.6 \times 981 \times 22400}{273} = 8.318 \times 10^7 \text{ ergs per gm-mol per } ^\circ A$$

$$\therefore = 8.318 \text{ joules per gm-mol per } ^\circ A.$$

Since 1 Calorie = 4.2 joules

$$\therefore R = \frac{8.318}{4.2} = 2 \text{ cal/gm mole/} ^\circ A \quad (\text{approx})$$

In the M.K.S. system, Normal pressure

$$= 1.014 \times 10^5 \text{ Newtons/m}^2$$

$$T = 273^\circ A$$

Volume of one Kilo-Mol. of gas = 22.4 m³

$$\therefore R = \frac{1.014 \times 10^5 \times 22.4}{273} = 8310 \text{ joules/Kilo-mol/} ^\circ A$$

$$= 2 \text{ K-cal/Kilo-mol/} ^\circ A$$

as one Kilo-cal = 4200 joules

If the pressure is expressed in kg/m² instead of Newtons/m², the value of R would be

$$= \frac{8310}{9.81} = 847 \text{ Kg-m/k-mol/} ^\circ A$$

Gram Molecular weight of a substance is the molecular wt. expressed in grams. Similarly kilo-gram molecular wt. and Pound Molecular weight are molecular wts. expressed in kgms and pounds respectively. The above quantities are some times called as gm-mol, the K-mol-lb-mol.

Some times the Universal gas equation is expressed in terms of Avagadro's Number (N) and Boltzmann constant (k).

3.13. Avogadro's Number (N). The number of molecules in one gm. mole of a gas is called the Avagadro's number. The number is constant for all gases and its value is

$$N = 6.02 \times 10^{23} \text{ per gm-mol.}$$

$$= 6.02 \times 10^{26} \text{ per k-mol.}$$

3.14. Boltzmann Constant (k). The ratio of universal gas constant R and Avagadro's number N is called as the Boltzmann constant (k). Its numerical value is

$$k = 1.38 \times 10^{-16} \text{ ergs per degree/molecule}$$

$$= 1.38 \times 10^{-23} \text{ joules/degree per molecule.}$$

From universal gas equation we have

$$\therefore PV = RT = N \cdot \frac{R}{N} \cdot T$$

$$\therefore PV = NkT \quad \text{where } k = \frac{R}{N}$$

$$\text{or } \frac{PV}{N} = kT \quad \text{or} \quad Pv = kT$$

where v = Volume of one molecule of a gas.

3.15. Variation of Density of a gas. Let ρ_1 be the density and V_1 volume of a given mass of a gas at a pressure P_1 and absolute temperature T_1 . Also let ρ_2, V_2, P_2 be the corresponding values at absolute temperature T_2 . Now from gas equation we have

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

As density of a gas at a given pressure and temperature varies inversely as its volume, then,

$$\rho_1 \propto \frac{1}{V_1} \text{ and } \rho_2 \propto \frac{1}{V_2}$$

Substituting the values in the gas equation, we have

$$\frac{P_1}{T_1 \rho_1} = \frac{P_2}{T_2 \rho_2}$$

if $P_1 = P_2$ then, from above equation

$$\frac{\rho_1}{\rho_2} = \frac{T_2}{T_1}$$

Hence the density of a gas at constant pressure varies inversely as the absolute temperature.

If $T_1 = T_2$ then, from the above equation

$$\frac{P_1}{\rho_1} = \frac{P_2}{\rho_2}$$

$$\text{or } \frac{\rho_1}{\rho_2} = \frac{P_1}{P_2}$$

Hence the density of a gas at constant temperature varies directly as the pressure.

Example. 13. 10 lbs. of air under a pressure of 1000 lbs/sq. inch has a temperature of 140°F . Find the volume occupied. Given $r = 53.37$ ft. lb. per $^\circ\text{F}$ for 1 lb. of air.

(A. M. I. E.)

$$P = 1000 \times 144 \text{ lbs/sq. ft.}$$

$$T = 460 + 140 = 600^\circ\text{R}$$

$$m = 10 \text{ lbs.}$$

$$r = 53.37 \text{ ft. lb. per } ^\circ\text{F per lb.}$$

$$V = ?$$

Applying, the equation

$$PV = mrT \quad \text{we have}$$

$$1000 \times 144 \times V = 10 \times 53.37 \times 600$$

$$\therefore V = \frac{10 \times 53.37 \times 600}{1000 \times 144} = 2.224 \text{ c. ft.}$$

Example. 14. A litre of air at 0°C and under atmospheric pressure weighs 1.2 gm. Find the mass of air required to produce at 18°C a pressure of 3 atmospheres in a volume of 75 c.c. (A. M. I. E.)

$$\text{Case I } P_1 = 1 \text{ atmosphere} = 1.013 \times 10^6 \text{ dynes/cm}^2$$

$$T_1 = 273^\circ\text{A}, \quad V_1 = 1 \text{ litre} = 1000 \text{ c.c.}$$

$$m = 1.2 \text{ gm.}$$

Applying equation $P_1V_1 = m_1rT_1$

$$1.013 \times 10^6 \times 1000 = 1.2 \times r \times 273$$

$$\therefore r = \frac{1.013 \times 10^6 \times 1000}{1.2 \times 273} = 3.12 \times 10^6$$

$$\text{Case II } P_2 = 3 \text{ atmospheres} = 3 \times 1.013 \times 10^6 \text{ dynes/cm}^2$$

$$T_2 = -18 + 273 = 255^\circ\text{A}$$

$$V_2 = 75 \text{ c.c. and } m_2 = ?$$

Again the equation $P_2V_2 = m_2rT_2$

$$\text{or } m_2 = \frac{P_2V_2}{rT_2} = \frac{3 \times 1.013 \times 10^6 \times 75}{3.12 \times 10^6 \times 255} = 0.288 \text{ gm.}$$

Example. 15. 30 cm³ of Hydrogen were collected in a tube over mercury at 28°C when the barometer stood at 75.8 cm. If the mercury inside the tube was 2 cm. higher than outside, calculate the volume of the gas at N.T.P. (A. M. I. E.)

$$P_1 = \text{The pressure of Hydrogen gas collected over mercury} \\ = 75.8 - 2 = 73.8 \text{ cm. of mercury}$$

$$V_1 = \text{Volume of the gas} = 30 \text{ cm}^3$$

$$T_1 = \text{Temperature} = 273 + 28 = 301^\circ\text{A}$$

$$P_2 = \text{Pressure at N.T.P.} = 76 \text{ cm. of Mercury}$$

$$T_2 = \text{Temperature at N.T.P.} = 273^\circ\text{A}$$

$$V_2 = \text{Volume of the gas at N.T.P.} = ?$$

Applying gas equation, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\therefore V_2 = \frac{P_1 V_1}{T_1} \times \frac{T_2}{P_2} = \frac{73.8 \times 30}{301} \times \frac{273}{76} \\ = 26.5 \text{ cm.}^3$$

Example. 16. A litre of dry air weighs 1.293 gms. at N.T.P., Find the temperature at which a litre of air will weigh 1 gm., when the pressure is 72 cm.

Initial volume of air $V_1 = 1 \text{ litre} = 1000 \text{ c.c.}$

Initial temperature $T_1 = 273^\circ A$

Initial pressure $P_1 = 76 \text{ cm. of mercury}$

Let $T_2^\circ A$ be the temperature at which 1 litre of air will weigh 1 gm.

\therefore Volume of 1 gm. of air $= 1 \text{ litre} = 1000 \text{ c.c.}$

Hence Volume of 1.293 gms. of air at $T^\circ A = 1000 \times 1.293 = 1293 \text{ c.c.}$

$\therefore V_2 = 1293 \text{ c.c.}$

$P_2 = 72 \text{ cm. of mercury}$

Using General gas equation, we have

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or

$$T_2 = \frac{P_2}{P_1} \cdot \frac{V_2}{V_1} \times T_1 \\ = \frac{72}{76} \times \frac{1293}{1000} \times 273 = 335.4^\circ A \\ = 335.4 - 273 = 62.4^\circ C$$

Example. 18. Find the mass of a litre of a moist air at a temperature of $32^\circ C$ and a pressure of 758.2 m.m., the dew point being $15^\circ C$. The saturation pressure of aqueous vapour at $32^\circ C$ is 12.7 m.m. The density of dry air at N.T.P. is 1.293 gm/litre. (A.M.I.E.)

According to Dalton's Law of partial pressures, the total pressure is due to both air and water vapour.

$$\therefore \text{Pressure exerted by air alone } P_1 = 758.2 - 12.7 \\ = 745.5 \text{ m.m.}$$

Volume at $32^\circ C$ and at pressure 745.5 m.m.

$V_1 = 1 \text{ litre}$

Temperature $T_1 = 273 + 32 = 305^\circ A$

Volume at N.T.P., $V_2 = ?$

Normal Temp. $T_2 = 273^\circ A$

Normal pressure $P_2 = 760 \text{ m.m.}$

Applying General gas equation, we have

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{745.5 \times 1}{305} = \frac{760 \times V_2}{273}$$

or
$$V_2 = \frac{745.5}{760} \times \frac{273}{305}$$

$$= 0.878 \text{ litre}$$

Density of air at N.T.P. = 1.293 gm./litre

\therefore Mass of this volume of air at N.T.P.

$$= 0.878 \times 1.293$$

$$= 1.136 \text{ gm.}$$

Example. 18. Two glass bulbs A and B of 400 c.c. and 200 c.c. are connected by a narrow tube of negligible volume. The apparatus is filled with air at 0°C and 76 cm. of Hg. pressure and sealed off. If the temperature of the glass bulb A is now raised to 100°C . Find (i) the new pressure in the system (ii) the mass of air which is transferred from one bulb to the other during heating. Take density of air at N.T.P. as 1.29 gm/litre.

The mass of the air in the two bulbs remains constant before and after heating.

Before heating. From the equation $PV = mRT$, we have

$$\text{Mass in bulb A, } m_a = \frac{P_a V_a}{RT_a} = \frac{76 \times 400}{273 \times R}$$

$$\text{Mass in bulb B, } m_b = \frac{P_b V_b}{RT_b} = \frac{76 \times 200}{273 \times R}$$

$$\therefore \text{Total mass } m = m_a + m_b = \frac{76 \times 600}{273 \times R} \quad \dots (i)$$

After heating. When the temperature of the bulb is raised to 100°C , the new pressure in both the bulbs becomes P .

$$\text{Mass in bulb A, } m'_a = \frac{P \times 400}{373 \times R}$$

$$\text{Mass in bulb B, } m'_b = \frac{P \times 200}{273 \times R}$$

$$\text{Total mass in both bulbs } m \quad m'_a + m'_b = \frac{P}{R} \left[\frac{400}{373} + \frac{200}{273} \right] \dots (ii)$$

As total mass before and after heating remains constant.

$$\frac{76 \times 600}{273R} = \frac{P}{R} \left[\frac{400}{373} + \frac{200}{273} \right]$$

$$= \frac{P}{R} \left[\frac{(400 \times 273 + 200 \times 373)}{373 \times 273} \right]$$

$$\begin{aligned} \text{or } P &= \frac{76 \times 600 \times 373}{100 (1092 + 746)} \\ &= \frac{76 \times 6 \times 373}{1878} = 92.6 \text{ cm. of Hg.} \end{aligned}$$

(ii) For bulb A

$$m_a = \frac{76 \times 600}{273 \times R} \text{ at N.T.P.}$$

$$m'_a = \frac{92.6 \times 400}{373 \times R} \text{ at } 100^\circ\text{C.}$$

$$\therefore \frac{m'_a}{m_a} = \frac{92.6}{76} \times \frac{273}{373} = 0.89$$

At N.T.P 1 litre means 1000 c.c. and 1000 c.c. of air have mass of 1.29 gm., hence 400 c.c. have mass of $= \frac{1.29}{1000} \times 400 = \frac{1.29}{2.5} = 0.515 \text{ gms.}$

$$\therefore m_a = 0.515 \text{ gms.}$$

$$\text{and } m'_a = 0.89 m_a$$

$$\begin{aligned} \therefore \text{mass transferred} &= m_a - m'_a = m_a - 0.89 m_a \\ &= 0.515 - 0.89 \times 0.515 \\ &= 0.055 \text{ gm.} \end{aligned}$$

3.16. Work done by a gas during expansion. Consider a certain quantity of a gas enclosed in a cylinder fitted with a moveable and frictionless piston of area A as shown. Let the initial volume of the gas be V_1 . Suppose the gas is heated then both its temperature and

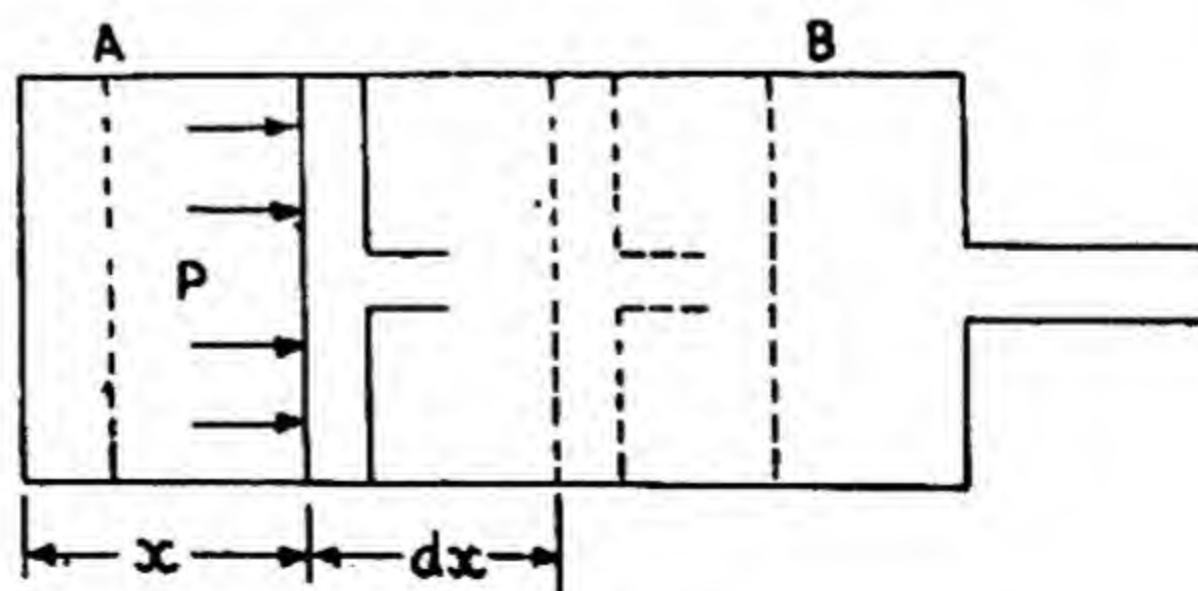


Fig. 3.5.

volume will increase but any tendency for the pressure to increase will

be counter-balanced by the outward movement of the piston. Hence during the process of heating the pressure of the gas remains constant and equal to the external pressure P and gas expands to volume V_2 .

Let during the expansion of the gas the piston moves out through a small distance dx .

Then work done by the gas

$$\begin{aligned} dW &= \text{Force acting on the piston} \times \text{distance moved} \\ &= (\text{Pressure } (P) \times (\text{Area of the piston}) \times dx \\ &= P \times A \times dx \\ &= P \times (Adx) \end{aligned}$$

But $Adx = \text{increase in volume} = dV$

\therefore Work done, $dW = PdV$

If the volume of the gas changes by a finite amount from V_1 to V_2 , then

Total work done, $W = P (V_2 - V_1)$

(i) If P is in Nts/m^2 and dV in m^3 , then work done is in **Joules**.

(ii) If P is in dynes/cm^2 and dV in cm^3 then work done is in **Ergs**.

When the gas expands as in this case the work is said to be done by the gas (+ve work done) whereas if the gas is allowed to compress the work is said to be done on the gas (-ve work done).

The expansion or compression of a gas can be represented on a graph drawn between P and V , pressure P is taken along the ordinate and the volume V is taken along the abscissa. This diagram is known as P - V diagram or Indicator diagram.

When the pressure is constant, the P - V diagram is the straight line indicated by aa' as shown in Fig. 3.7 where constant pressure is equal to AD or BC . If the volume of the gas changes from a value represented by OD to a value represented by OC then

$$\text{Change in volume} = OC - OD = DC$$

Thus work done

$$\begin{aligned} &= P \times \text{change in volume} \\ &= P \times (V_2 - V_1) \\ &= \text{Area } ABCD \end{aligned}$$

Hence the work done is given by the shaded area between the expansion line and volume axis.

Now let the gas expand on heating according to the PV curve AB from an initial volume V_1 to a final volume

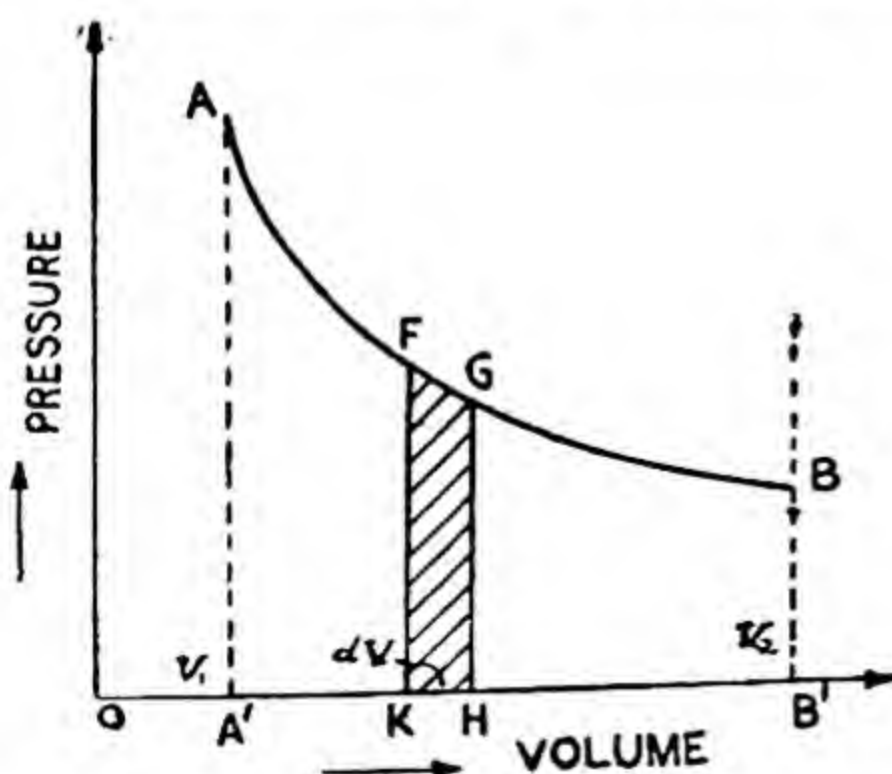


Fig. 3.6

V_2 corresponding to positions A and B of the piston. Let P be the pressure and V the volume of the gas for any position of the piston x from the bottom of the cylinder. Although the pressure changes from a value represented by KF to a value HG , when the volume increases from OK to OH , we can imagine the pressure to be kept constant while a very small change of volume dV is made.

Then the work done by the gas is given by

$$dW = PdV$$

= work done by the gas in expansion from OK to OH

= Shaded Area of $KFGH$

∴ Total work done by the gas when its volume changes from V_1 to V_2

$$W = \int_{V_1}^{V_2} PdV$$

= Total area under the curve AB .

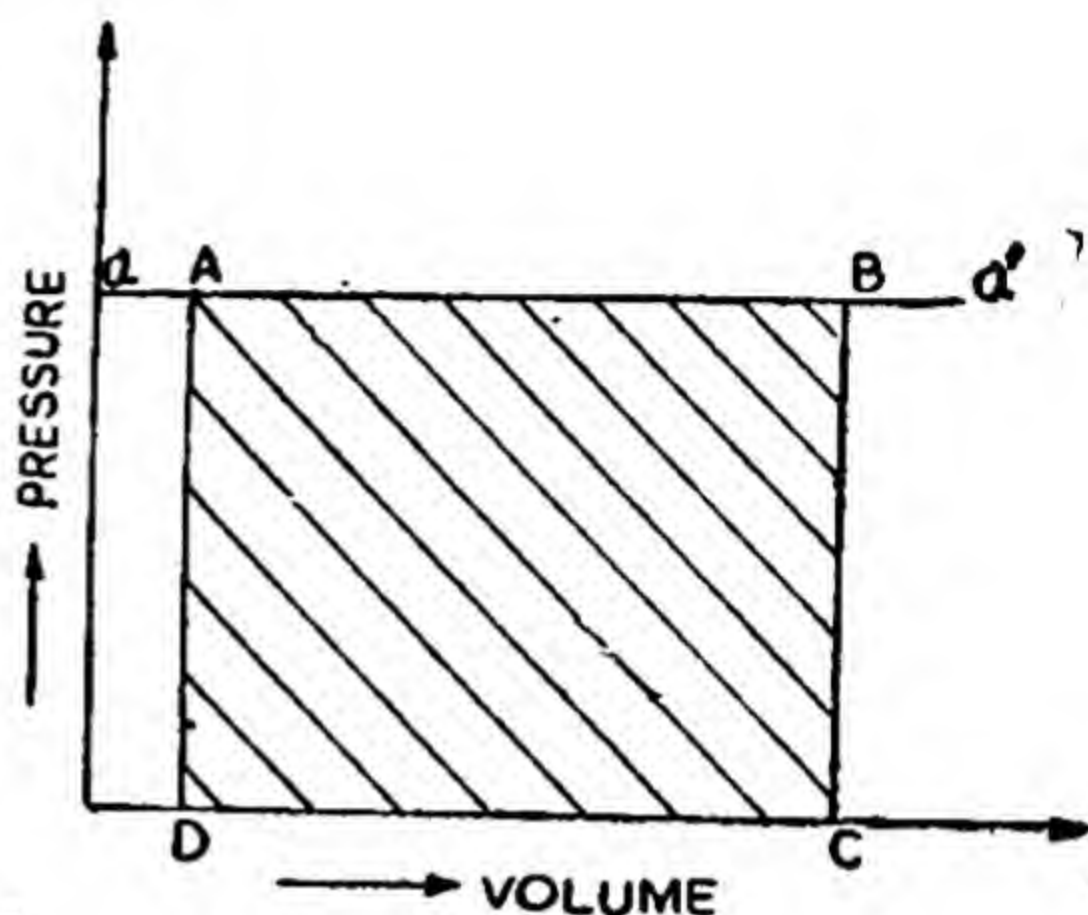


Fig. 3.7

We can thus formulate a general statement :

The work done by a gas is equal to the area between its $P-V$ diagram and the volume axis, taken between the limits corresponding to its initial and final volumes.

Example. 19. A cylinder contains 3 litres of air at 2 atmospheric pressure and at $300^\circ A$. The air is carried through the following operations, (a) heated at constant pressure to $500^\circ A$ (b) cooled at constant volume to $250^\circ K$ (c) cooled at constant pressure to $150^\circ A$. (d) heated at constant volume to $300^\circ A$. Show each process in pressure volume diagram giving the numerical values of P and V at the end of each process. Calculate the net work done. (A.M.I.E.)

Let at the initial condition of the air ($P_1 = 2$ atmospheres, $V_1 = 3$ litres and $T_1 = 300^\circ A$) be represented by A in Fig. 3.6. Let us consider each operation separately.

(a) Line AB represents heating of air at constant pressure. Since pressure remains constant, applying Charle's law we get

$$\frac{V_2}{T_2} = \frac{V_1}{T_1}$$

$$\text{or } \frac{V_2}{V_1} = \frac{T_2}{T_1}$$

$$\therefore V_2 = \frac{T_2}{T_1} \times V_1 = \frac{500}{300} \times 3 = 5 \text{ liters.}$$

(b) Line BC represents cooling at constant volume (Fig. 3.7). Hence applying Gay—Lussac's Law, we have

$$\frac{P_3}{T_3} = \frac{P_2}{T_2}$$

$$\text{or } \frac{P_3}{P_2} = \frac{T_3}{T_2}$$

$$\therefore P_3 = \frac{T_3}{T_2} \times P_2 = \frac{250}{500} \times 2 = 1 \text{ atm.}$$

(c) Line CD represents cooling at constant pressure (Fig. 3.7). Hence applying Charle's Law again, we have

$$\frac{V_4}{T_4} = \frac{V_3}{T_3}$$

$$\therefore V_3 = V_4 \frac{T_3}{T_4} = 5 \times \frac{150}{250} = 3 \text{ litres.}$$

This volume is equal to the original volume V_1 .

(d) Line DA represents heating at constant volume (Fig. 3.7). It is obvious that the air returns to the initial condition after this process.

Now the net work done by air in the whole operation

= Area enclosed by the shaded rectangle $ABCD$.

= $AB \times AD$

$$AB = DC = 5 - 3 = 2 \text{ litres} = 2 \times 10^{-3} \text{ m}^3$$

$$AD = BC = 2 - 1 = 1 \text{ atmosphere} = 1.013 \times 10^5 \text{ Nt/m}^2$$

$$\therefore \text{Work done} = 2 \times 10^{-3} \times 1.13 \times 10^5 \text{ joules,}$$

$$= 202.6 \text{ joules}$$

Expected Questions

1. (a) Define the meaning of the terms (i) coefficient of increase of pressure at constant volume (ii) coefficient of volume at constant pressure.

(b) Prove that in the case of a perfect gas the pressure coefficient is equal to the volume coefficient. Explain how this concept leads to the concept of absolute zero of temperature. (A.M.I.E.)

2. (a) Explain what is meant by a perfect or ideal gas. In what respects do ordinary gases differ from a perfect gas?

(b) State the various laws applicable to a perfect gas.

3. What is meant by the characteristic gas equation? Deduce the equation $PV = mRT$ for a gram molecule of a gas from Boyle's and Charle's Laws. (A.M.I.E.)

4. (a) What are the units in which gas constants r or R are measured.

(b) What is the numerical value of gas constant in,

(i) Joules/kgm.—mole— $^{\circ}K$

(ii) ergs/gm.—mole— $^{\circ}K$.

5. What is meant by gm.-mole of a gas. What is its value for oxygen. What is the volume occupied by one gm.-molecule of any gas at N.T.P.

6. (a) Deduce the equation, $PV = mRT$ assuming Boyle's Law and Charle's Law. What is the Physical significance of R .

(b) Show that R represents the external work done by a unit mass of the gas when heated at constant pressure through $1^{\circ}C$. (A.M.I.E.)

7. (a) How does the density of a gas depend on its pressure and temperature.

(b) What are (i) Boltzmann's constant (ii) Avogadro's number? What are their approximate values?

CHAPTER IV

SPECIFIC HEAT OF SOLIDS AND LIQUIDS

4.1. Introduction. Heat is a form of energy and as such it is a measurable quantity. So far we have concerned ourselves with the measurement of temperature and the changes produced in volume by heat without any idea to measure the quantity of heat required in a particular process. In this chapter, we will discuss the measurement of heat and also the conditions upon which the transfer of heat from one body to another depends. *The process of measuring the quantities of heat is called calorimetry.*

4.2. Units of Heat. To measure the quantity of heat the common units used are (i) **Calorie (cal)** (ii) **Kilo calorie (k. cal)** (iii) **British thermal unit (B. Th. U.)** (iv) **Therm** (v) **Centigrade heat unit (C. H. U.)**

Calorie. This is the unit of heat on the *C. G. S.* system. *It is the quantity of heat required to raise the temperature of 1 gram of water through 1°C .*

It may be pointed out that the quantity of heat required to raise the temperature of 1 gram of water through 1°C is not the same at all temperatures. For example, the heat required to raise the temperature of 1 gm. of water from 10°C to 11°C is not the same as that required to heat it from 40°C to 41°C . For this reason if we take one gm. of water and raise its temperature from 0°C to 100°C (at standard pressure) and then divide this quantity of heat by 100, we get what is called as the **mean calorie**. It has been found that the value of this **mean calorie** is equal to the amount of heat required to raise the temperature of one gm. of water from 14.5°C to 15.5°C . For all engineering purposes this unit is generally used. It is known as 15°calorie .

Kilo-Calorie. This is the unit of heat in *M.K.S.* system. *It is the amount of heat required to raise the temperature of 1 kilogram of water through 1°C .*

$$1 \text{ Kilo Calorie} = 1000 \text{ Calories.}$$

4.3. British Thermal unit (B. Th. U). This is the unit of heat in *F.P.S.* system. *It is the amount of heat required to raise the temperature of one pound of water through 1°F .*

Since 1 lb of water = 454 gms and $1^{\circ}\text{F} = \frac{5}{9}^{\circ}\text{C}$.

$$\therefore 1 \text{ B. Th. U} = 454 \times \frac{5}{9} = 252 \text{ Calories.}$$

Another bigger unit in the *F.P.S.* system is called **Therm** which is equal to 10^6 B. Th. U.

$$\therefore 1 \text{ Therm} = 100,000,0 \text{ B.Th.U.}$$

4.4. Centigrade Heat unit (C.H.U.) *It is the amount of heat required to raise the temperature of 1 lb of water through 1°C .*

$$1 \text{ C.H.U.} = \frac{9}{5} \text{ B.Th. U.} = 1.8 \text{ B. Th.U} = 1.8 \times 252 = 454 \text{ Calories.}$$

4.5. Specific heat. When a body is heated, it absorbs heat and when it is cooled it loses heat. It is found that a certain mass of a substance requires a definite quantity of heat to raise its temperature through a certain range. This quantity of heat is different for different substances. Hence the quantity of heat (Q) necessary to raise the temperature of the body

(i) is proportional to the mass of the body (m)

$$Q \propto m$$

(ii) is proportional to the rise in temperature (t),

$$Q \propto t$$

Combining both these factors, we have

$$Q \propto mt$$

or

$$Q = mSt$$

where S is the constant of proportionality. Its value depends upon the nature of the substance but is independent of Q , m and t . This constant S is known as **specific heat** of the substance and is equal

$$\text{to } S = \frac{Q}{mt}$$

If $m = 1$ gm. and $t = 1^{\circ}\text{C}$ Then

$$Q = S$$

Hence specific heat of a substance is equal to the quantity of heat in calories required by 1 gm. of that substance for heating it through 1°C . Its unit is calories/gm/ $^{\circ}\text{C}$.

It can also be defined as the quantity of heat measured in kilocalorie, for raising the temperature of 1 kg. of the substance through 1°C . In this case its unit is $\text{K-cal/kg/}^{\circ}\text{C}$.

The units chosen in *F. P. S.* system are *B. Th. U./lb°/F* and *C. H. U./lb/°C* depending upon the scale of temperature used.

Let m gm of a substance of specific heat S_1 require Q_1 units of heat when it is heated through $t^\circ\text{C}$.

$$\text{then } Q_1 = mS_1t \quad \dots(i)$$

If m gm. of water of a specific S_2 is heated through the same range of temperature, then it will require Q_2 units of heat. In this case

$$Q_2 = mS_2t \quad \dots(ii)$$

From (i) and (ii) we have

$$\frac{Q_1}{Q_2} = \frac{S_1}{S_2}$$

For water the value of specific heat is always unity which is the maximum value. Thus putting $S_2 = 1$ in the above equation, we have

$$S_1 = \frac{Q_1}{Q_2}$$

Hence **Specific heat** of a substance is the *ratio of the quantity of heat required to raise the temperature of a certain mass of the substance through a certain range of temperature to the amount of heat required to heat the same mass of water through the same range of temperature.* Thus specific heat

$$S = \frac{\text{Quantity of heat required to raise the temperature of a given mass of a substance through a certain range}}{\text{Quantity of heat required to raise the temperature of the same mass of water through the same range}}$$

$$\text{or } S = \frac{\text{Quantity of heat required to raise the temperature of unit mass of a substance through } 1^\circ\text{C}}{\text{Quantity of heat required to raise the temperature of unit mass of water through } 1^\circ\text{C}}$$

The specific heat expressed as such is only a ratio and has no units.

Specific heat of different substances is different. Specific heat of water is maximum (unity) and so for the same mass and temperature it has maximum energy. Out of liquids mercury has least specific heat. In solid state specific heat is less than that of liquid of same material. Specific heat of ice is much less than that of water. Specific heat of substances generally increases with increase of temperature (described later on). In an experiment mean specific heat is found out.

4.6. Thermal capacity. *The thermal capacity of a body is equal to the amount of heat required to raise the temperature of the body through 1°C .*

If a body of mass m and specific heat S is heated through 1°C then the amount of heat required by it is equal to its thermal capacity.

Thermal capacity $= mS \times 1$ calories.

The units of the thermal capacity are $\text{cal}/^\circ\text{C}$, $\text{k-cal}/^\circ\text{C}$, $\text{B. Th. U.}/^\circ\text{F}$ and $\text{C. H. U.}/^\circ\text{C}$ depending upon the unit of mass (whether gm. or kgm or lb) and scale of temperature (whether 1°C or 1°F) chosen.

4.7. Water equivalent *The water equivalent of a body is the amount of water which absorbs or loses the same amount of heat as is done by the body when its temperature is raised or lowered through 1°C .*

Let m be the mass of the body and S its specific heat, then heat required to raise the temperature through 1°C is equal to mS calories. This quantity of heat will raise the temperature of mS gms of water through 1°C , since specific heat of water is unity.

\therefore water equivalent $= mS$ gms.

The units of water equivalent are gm, kgm. or lb.

Thus we see that the water-equivalent is numerically equal to its thermal capacity but former (**water equivalent**) is measured in **gms.** while the latter (**Thermal Capacity**) is measured in **Calories**.

Quantity of heat required to heat a body. Let S be the specific heat of a given material. Then the amount of heat required to raise the temperature of m gms. of that material through $t^\circ\text{C}$ is given by

$$Q = mSt.$$

The same relation will also give the quantity of heat lost by a body when it is allowed to cool through a certain range of temperature. Then Q will be the amount of heat lost by the body and t , the fall in temperature.

4.8. Principle of measurement of heat. When two substances at different temperatures are mixed together, heat flows from the substance at a higher temperature to the substance at a lower temperature till the temperatures of the two become the same. If during this process no heat has been gained from or given to any outside body and there is no chemical action in the mixture, then *the heat lost by the hot body must be equal to the heat gained by the cold body.* Thus

Heat lost = Heat gained.

The above equation is termed as the principle of **calorimetry**.

Example. 1. A boiler in a heating system is 50% efficient. The boiler is filled with water at 65°F . After burning the coal which liberates 50,000 B. Th. U. the water has a temperature of 210°F . What is the weight of water in the boiler? (A.M.I.E.)

Quantity of heat $Q = mSt$ where S is the specific heat of water

For water $S=1$

$$\therefore Q = mt.$$

Note [Q is in *B. Th. U.* if m is in lbs and t in $^{\circ}F$.]

Total heat produced = 50,000 *B. Th. U.*

$$\text{Heat utilised} = \frac{50}{100} \times 50,000 = 25000 \text{ B. Th. U.}$$

$$\therefore 25000 = m(210 - 65) = m \times 145,$$

$$\therefore m = \frac{25000}{145} = 172.4 \text{ lbs.}$$

Example. 2. In two experiments, 610 gm. of water are heated from $14^{\circ}C$ to $94^{\circ}C$ and 30 lb 8 oz of water are heated from $34^{\circ}F$ to $89^{\circ}F$. In which case is the greater quantity of heat supplied.

(A. M. I. E.)

(i) Mass of water heated = 610 gms.

Rise in temp = $80^{\circ}C$.

Heat supplied $H_1 = m S t = 610 \times 1 \times 80 = 48800 \text{ cal.}$

(ii) Mass of water heated = 3.5 lbs.

Rise in temperature = $55^{\circ}F$.

\therefore Heat supplied $H_2 = m S t = 3.5 \times 1 \times 55 = 192.5 \text{ B. Th. U.}$

But 1 *B. Th. U.* = 252 calories.

$\therefore H_2 = 192.5 \times 252 = 48510 \text{ calories.}$

Hence. $H_1 > H_2$ i.e. more heat is supplied in the first case.

4.9. Methods of measuring specific heat of solids.

The following methods are available for the determination of the specific heat of solids.

1. Method of Mixtures.
2. Method of Fusion of ice (Bunsen's Ice Calorimeter)
3. Joly's Steam Calorimeter.
4. Nernst and Lindemann's Vacuum Calorimeter.

1. Methods of mixtures. The specific heat of a solid such as lead shots or copper can be easily determined by a simple method known as the **method of mixtures**. The solid whose specific heat is to be determined is placed in the copper tube of the hypsometer and mouth of the tube is closed with a cork having a hole. Through the hole a thermometer is passed so that its bulb and a part of its stem are surrounded by the solid. This tube is inserted into the hypsometer as shown in Fig. 4.1(i) and is heat to a constant temperature of the steam.

In the meantime, a clean and dry calorimeter, well polished from outside is weighed along with its stirrer. The calorimeter is then

filled nearly one-third with cold water having a temperature about 10°C below the room temperature and weighed again. The tem-

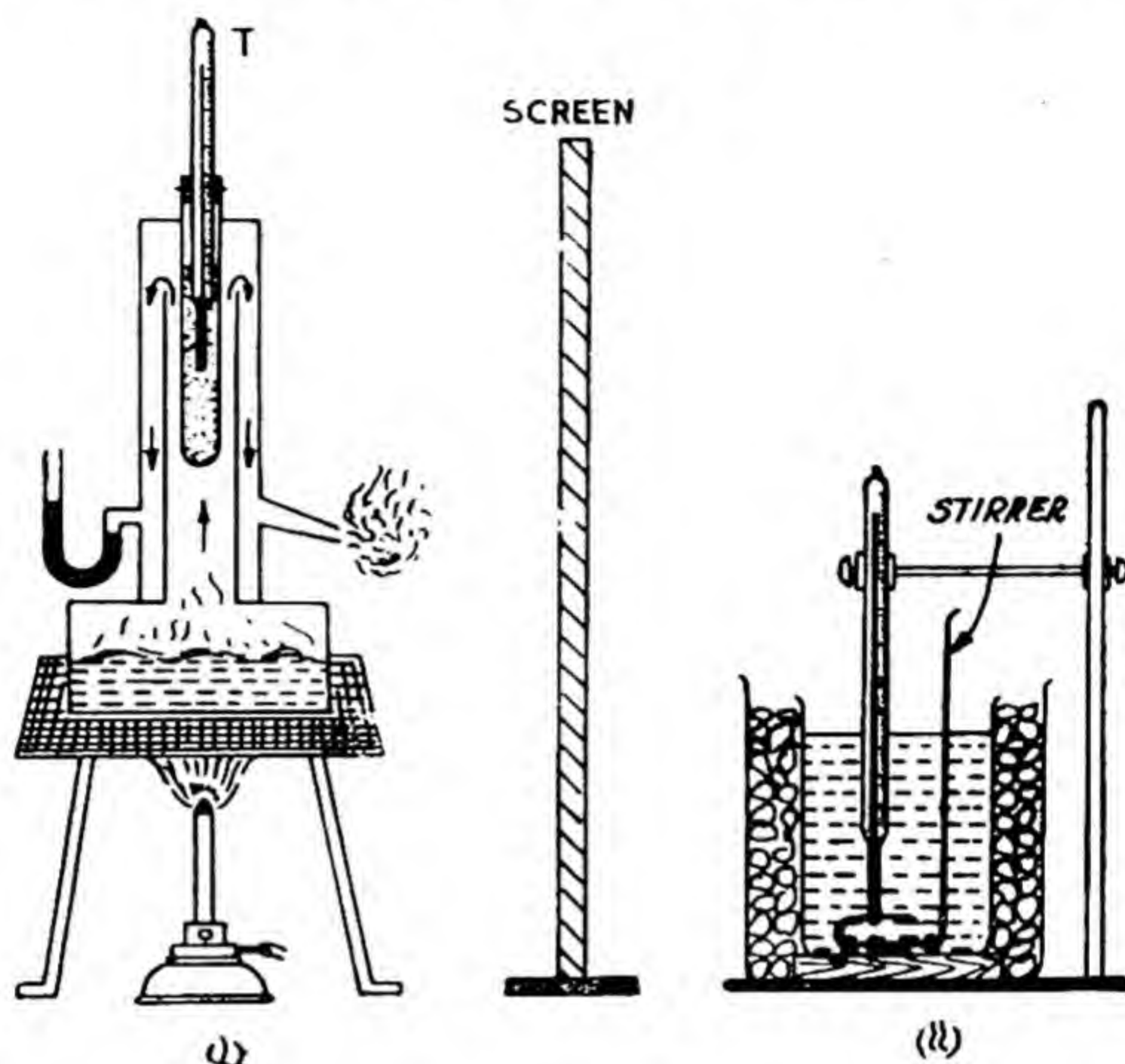


Fig. 4.1.

perature of heated solid in the hypsometer is noted when it becomes constant. The temperature of the cold water in the calorimeter is now noted and the hot solid is quickly transferred into the calorimeter. The mixture is well-stirred and its final maximum temperature is recorded. The calorimeter is once again weighed with its contents. With the help of the above observations, the specific heat of the solid can be calculated as follows.

Let the mass of the calorimeter and stirrer $= m_1$ gms.

Mass of the cold water taken in the calorimeter $= m$ gms.

Mass of hot solid added, $= M$ gms.

Initial temperature of cold water and calorimeter $= t^{\circ}\text{C}$

Steady temperature of hot solid $= T^{\circ}\text{C}$

Final temperature of the mixture $= \theta^{\circ}\text{C}.$

Let S be the specific heat of the solid and s that of the material of the calorimeter.

Heat lost by hot solid in cooling from $T^{\circ}\text{C}$ to $\theta^{\circ}\text{C}.$

$$= MS (T - \theta) \text{ cal.}$$

Heat gained by the cold water, calorimeter and stirrer in raising the temperature from $t^{\circ}\text{C}$ to $\theta^{\circ}\text{C}$.

$$= m(\theta - t) + m_1 s(\theta - t) \\ = (m + m_1 s)(\theta - t)$$

Since Heat lost = Heat gained

$$\therefore MS(T - \theta) = (m + m_1 s)(\theta - t)$$

$$\text{or specific heat of the solid } S = \frac{(m + m_1 s)(\theta - t)}{M(T - \theta)}$$

Example. 3. A piece of iron of mass 100 gms is rapidly removed from a furnace and immersed in a calorimeter weighing 46 gms. The furnace temperature was 98.5°C and the calorimeter contained 85.5 gms of water at 15°C . The final temperature of the contents of the calorimeter was found to be 22°C . Calculate the specific heat of iron. The specific heat of the calorimeter is 0.1.

(A. M. I. E.)

Mass of iron $M = 100$ gms.

Temperature of iron $T = 98.5^{\circ}\text{C}$.

Mass of calorimeter, $m_1 = 46$ gms.

Mass of water $m = 85.5$ gms.

Temperature of water $t = 15^{\circ}\text{C}$.

Final temperature of the mixture $\theta = 22^{\circ}\text{C}$

Specific heat of the calorimeter $= 0.1$

Let S be specific heat of iron.

Fall in temperature of iron $= (T - \theta) = 98.5 - 22 = 76.5^{\circ}\text{C}$.

Rise in temperature of calorimeter and water
 $= (\theta - t) = 22 - 15 = 7^{\circ}\text{C}$

Heat lost by iron $= MS(T - \theta) = 100 \times S \times 76.5$ cal. ... (i)

Heat gained by calorimeter $= m_1 s(\theta - t) = 46 \times 0.1 \times 7 = 32.2$ cal.

Heat gained by water $= m(\theta - t) = 85.5 \times 7 = 598.5$ cal.

Total heat gained by calorimeter and water $= (m_1 s + m)(\theta - t)$
 $= 32.2 + 598.5 = 630.7$ cal ... (ii)

But Heat lost = Heat gained.

$$\therefore 100 \times S \times 76.5 = 630.7$$

$$\text{or } S = \frac{630.7}{7650} = 0.0825$$

Example. 4. A calorimeter weighs 200 gm. and contains 1000 gm of water at a temperature of 22°C . If 400 gm. of a mixture of copper and aluminium filings at a temperature of 100°C are put into the calorimeter and final uniform temperature of the whole is 26.5°C . Determine the mass of the aluminium filings.

[Specific heat of $Al = 0.218$.]

Mass of the calorimeter

$$m_1 = 200 \text{ gms.}$$

mass of water

$$m = 1000 \text{ gms.}$$

Temperature of water

$$t = 22^\circ C$$

Final temperature of the mixture

$$\theta = 26.5^\circ C.$$

Specific heat of the calorimeter

$$s = 0.093.$$

Wt of the mixture of copper and aluminium

$$M = 400 \text{ gms.}$$

Specific heat of Al ,

$$S' = 0.218.$$

$$\begin{aligned} \text{Heat absorbed by water and calorimeter} &= (m + m_1 s) (\theta - t) \\ &= (1000 + 200 \times 0.093) (26.5 - 22) \\ &= 1018.6 \times 4.5 = 4583.7 \text{ cal.} \end{aligned}$$

[**Note** Calorimeter is always of copper material hence specific heat of copper $s = 0.093$.]

Let w be the mass of aluminium filings in the mixture so that $(400 - w)$ is the mass of the copper filings,

$$\begin{aligned} \text{Heat lost by Aluminium} &= wS(T - \theta) = w \times 0.218 \times (100 - 26.5) \\ &= w \times 0.218 \times 73.5 \text{ cal.} \end{aligned}$$

$$\text{Heat lost by copper} = (400 - w) s \times (T - \theta)$$

$$\therefore \text{Heat lost by copper} = (400 - w) 0.093 (73.5)$$

$$\begin{aligned} \text{Total heat lost by mixture} &= w \times 0.218 \times 73.5 + (400 - w) \times 0.093 \times 73.5 \\ \text{of copper and Al. filings} &= 15.1w + 2809 - 6.85w \\ &= 9.25w + 2809. \end{aligned}$$

$$\text{Heat lost} = \text{Heat gained}$$

$$\therefore 9.25w + 2809 = 4583.7$$

$$\text{or } w = \frac{1774.7}{9.25} = 192 \text{ gms}$$

2. Bunsen's Ice Calorimeter. It is a method for determining the specific heat of a solid by using the phenomenon of fusion of ice.

The fact that ice *contracts* on melting was utilised by Bunsen in constructing a very delicate calorimeter known as **Bunsen's Ice Calorimeter**. It has been found that 1 gm. of ice at $0^\circ C$ occupies 1.0908 c.c. whereas 1 gm. of water at $0^\circ C$ has a volume of 1.00001 c.c. Hence the fact that one gm. of ice on melting decreases in volume by $(1.0908 - 1.00001) = 0.0907 \text{ c.c.}$ is used to find the correct weight of ice melted by the hot solid.

It consists of a wide glass tube B into the upper part of which a long thin walled test-tube A is fused. The lower end of the wide tube B is sealed at C to a narrow tube CD bent twice at right angles. The other end D of this tube terminates into a collar which is closed by a cork through which passes a bent piece of capillary tube of uniform bore. A scale S is attached to the horizontal part of this capillary tube so that volume between any two divisions is known accurately. The upper part of the wide tube B is filled with pure water from which dissolved air has been removed by boiling. The remaining part of the wide tube B and whole of the bent tube CD and also a part of the capillary tube are filled with pure dry mercury.

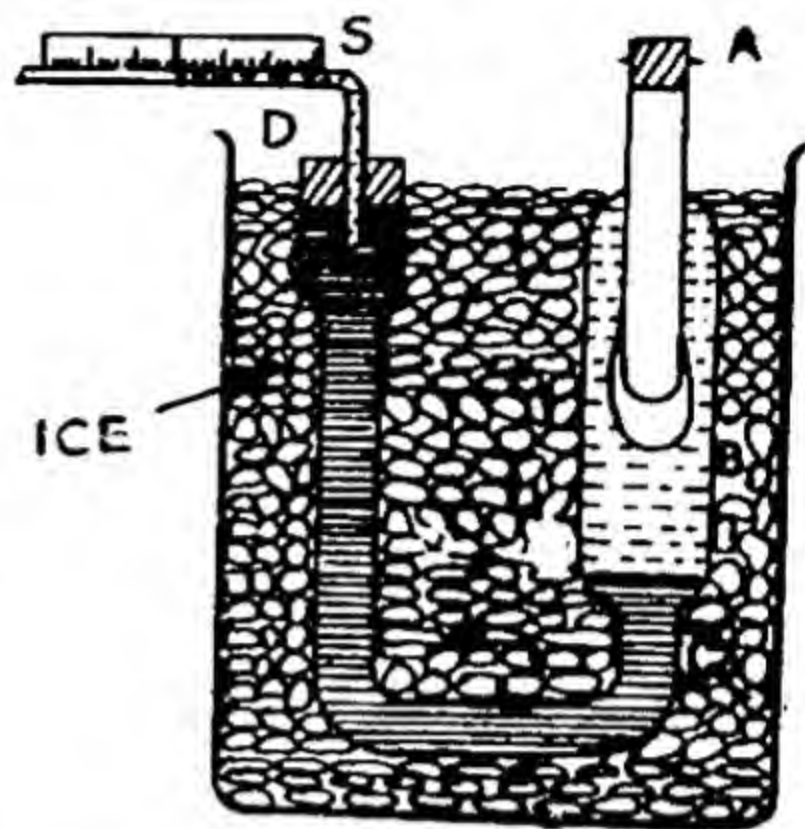


Fig. 4.2.

The apparatus is now placed in a vessel containing finely broken ice, so as to allow it to attain the temperature of ice. Some previously cooled ether is then poured into the tube A and air is blown into it in order to make it evaporate quickly. As ether evaporates its temperature falls below 0°C and some water in B is converted into ice and appears on the outside of tube A . During this process mercury level in the capillary tube will be found to have moved forward. When a thin layer of ice is formed round tube A , the ether is removed and ice cold water is introduced. Apparatus is still left in melting ice so that the temperature of the calorimeter and its content, is maintained at 0°C . This will be so if the mercury meniscus remains at a steady position which is read on the scale S .

Now the body whose specific heat is to be determined is taken and weighed. It is heated to a constant high temperature and is then suddenly dropped into the water in A and the tube is corked at once. The heat contained in the solid body will be given to the surrounding ice by the water contained in the tube and will melt part of it. This will continue till the temperature of the solid and water in the tube is again 0°C . With the melting of ice contraction in the volume takes place which causes the mercury meniscus in the capillary tube to move inwards. When the meniscus has been steady for some time its position is again read on the scale S . The difference in this reading and the previous reading gives the decrease in volume which has taken place. Let this be $v.c.c.$ Since 1 gm. of ice on melting decreases in volume by 0.0907 c.c. , the mass of the ice melted for a decrease in volume equal to $v.c.c.$ is given by

$$m = \frac{v}{0.0907}$$

If $L \text{ cal/gm.}$ is the latent heat of fusion of ice then heat gained

$$\begin{aligned} \text{by } m \text{ gms. of ice at } 0^\circ\text{C in melting} &= mL \\ &= \frac{L \cdot v}{0.0907} \end{aligned}$$

If M is the mass of the body, S its specific heat and t its initial temperature, then

Heat lost by the solid in cooling from $t^\circ\text{C}$ to $0^\circ\text{C} = MSt$ cal.s.

As this has fully been utilised in melting ice, we have

$$\begin{aligned} MSt &= \frac{Lv}{0.0907} \\ \therefore S &= \frac{Lv}{0.0907 \times Mt} \end{aligned}$$

Advantages.

1. It is very sensitive and accurate method.
2. This method is specially useful for solids which are available in small quantities.
3. The water equivalent of the apparatus does not enter into the calculations.
4. There is no radiation taking place as the whole apparatus is surrounded by ice which is a poor conductor of heat.
5. The apparatus can be used both for solids and liquids.

Example 5. *If one gram of ice at 0°C contracts by 0.091 c.c. on melting, calculate the mass of a metal of specific heat 0.112 heated to 100°C which when dropped into an ice calorimeter causes a decrease in volume of 0.0637 c.c.*

Decrease in volume of ice $v = 0.0637$ c.c.

Decrease in volume when 1 c.c. of ice melts
 $= 0.091$ c.c.

Let m be the mass of ice melted.

$$\therefore m = \frac{v}{0.091} = \frac{0.0637}{0.091} = 0.7 \text{ gm.}$$

Temperature of the metal, $t = 100^\circ\text{C}$

Specific heat of the metal, $S = 0.112$

Let M be the mass of the metal dropped into the ice calorimeter.

Heat lost by the metal $= MSt$
 $= M \times 0.112 \times 100$ cal.s.

Heat gained by ice $= mL = m \times 80$ cal.s.

Heat lost $=$ Heat gained

$$\therefore M \times 0.112 \times 100 = 0.7 \times 80$$

$$\begin{aligned} \text{or } M &= \frac{0.7 \times 80}{0.112 \times 100} \\ &= 5 \text{ gms.} \end{aligned}$$

Example 6. The density of ice is 0.93 gm. per c.c. at 0°C. A piece of metal weighing 150 gms. is heated to 100°C and is then placed in Bunsen's ice calorimeter. The decrease in volume is found to be 1.876 c.c. Calculate the specific heat of the metal, latent heat of water being 80.

$$\text{Density of ice at } 0^{\circ}\text{C} = 0.93 \text{ gm./c.c.}$$

$$\text{Volume of 1 gm. of ice} = \frac{1}{0.93} = 1.075 \text{ c.c.}$$

When this 1 gm. of ice melts, it forms 1 gm. of water whose volume is 1 c.c. In other words, when 1 gm. of ice at 0°C melts to water at 0°C, the contraction in volume is

$$1.075 - 1 = 0.075 \text{ c.c.}$$

$$\text{Contraction in volume as given} = 1.876 \text{ c.c.}$$

$$\begin{aligned} \therefore \text{mass of ice melted} &= \frac{1.876}{0.075} \\ &= 24.924 \text{ gms.} \end{aligned}$$

$$\begin{aligned} \text{Heat gained by ice for melting} &= mL \\ &= 24.924 \times 80 \text{ cal.} \end{aligned}$$

$$\text{Mass of the metal piece } M = 150 \text{ gms.}$$

$$\text{Temperature of the metal piece } t = 100^{\circ}\text{C}$$

Let S be the specific heat of the metal piece.

$$\begin{aligned} \text{Heat lost by the metal} &= MSt \\ &= 150 \times S \times 100 \text{ cal.} \end{aligned}$$

$$\text{Heat lost} = \text{Heat gained}$$

$$150 \times S \times 100 = 24.924 \times 80$$

$$\begin{aligned} \therefore S &= \frac{24.924 \times 80}{150 \times 100} \\ &= 0.1329 \end{aligned}$$

Example 7. A substance weighing 20 gms. and at 100°C was dropped into a Bunsen ice calorimeter and the liquid column in the capillary tube of 1 sq. m.m. in area, contracted through 5 cm. Find the specific heat of the substance.

Given that 1 gm. of ice on melting contracts by 0.09 c.c.

$$\text{Mass of the substance } M = 20 \text{ gms.}$$

$$\text{Temperature of the substance } t = 100^{\circ}\text{C}$$

$$\begin{aligned} \text{Contraction in length of the column of liquid } l &= 5 \text{ cm.} \end{aligned}$$

$$\begin{aligned} \text{Contraction in volume} &= a \times l \\ &= 0.01 \times 5 = 0.05 \text{ c.c.} \end{aligned}$$

$$\begin{aligned}\text{Mass of ice melted} &= \frac{v}{0.09_1} = \frac{0.05}{0.09} = \frac{5}{9} \text{ gm.} \\ &= 0.555 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{Heat gained by ice} &= m \times L \\ &= 0.555 \times 80 \\ &= 44.4 \text{ cal.}\end{aligned}$$

$$\begin{aligned}\text{Heat lost by the substance} \\ &= MSt = 20 \times S \times 100 \text{ cal.}\end{aligned}$$

$$\text{Heat lost} = \text{Heat gained}$$

$$2000 S = 44.4$$

$$\therefore S = \frac{44.4}{2000} = 0.022$$

Example 8. 20 gms. of water at 15°C are put into the tube of a Bunsen's ice calorimeter and it is observed that the mercury thread moves through 30 cm. 12 gm of a metal at 100°C are then placed in the tube and the mercury thread moves through 12 cm. Find the specific heat of the metal..

(U.P.B.)

- | | | |
|------|----------------------------------|--|
| (i) | Mass of water | = 20 gms. |
| | Specific heat of water | = 1 |
| | Initial temperature of water | = 15°C . |
| | Final temperature of water | = 0°C . |
| (ii) | Mass of metal | = 12 gms. |
| | Initial temperature of the metal | = 100°C . |
| | Final temperature of the metal | = 0°C . |
| | Specific heat of the metal | = S . |
| (i) | Heat lost by water | = Mass of water \times Specific heat \times rise in temp.
= $20 \times 1 \times 15 = 300$ Cals. |
| (ii) | Heat lost by metal | = $12 \times S \times 100$ Cals.
= $1200 S$ Cals. |

The movement of mercury thread for loss of 300 Calories = 30 cm.
The movement of mercury thread for loss of $1200 S$ Cals. = 12 cm.

$$\therefore \frac{300}{30} = \frac{1200S}{12}$$

$$\text{or } S = \frac{300}{30} \times \frac{12}{1200} = 0.1$$

Example 9. If the latent heat of fusion of ice is 80, and its density at 0°C is 0.917, find the travel of the mercury in the tube of a Bunsen ice Calorimeter, when 10 calories, are given to the ice, the diameter of the tube being, 0.4 cm.

(Lond. Univ.)

Quantity of heat supplied to ice $Q=10$ cal.

Amount of ice melted $m=\frac{Q}{L}$ gms.

Density of ice at 0°C $\rho=0.917$ gms/c.c.

\therefore Volume of ice melted $V_1=\frac{m}{\rho}$

Now 1 gm. of water has a volume of 1.000 c.c.

\therefore Volume of water formed $V=m$ cm³.

\therefore Diminution in volume due to melting $=V_1-V$

$$=\left(\frac{m}{\rho}-m\right)$$

$$=\frac{m}{\rho}(1-\rho)$$

$$=\frac{Q}{L\rho}(1-\rho)$$

Let the radius of the tube $=r$ cm. and the distance which the mercury recedes due to change in volume $=l$ cm.

\therefore Change in volume of the mercury in the tube $=\pi r^2 l$.

Hence $\pi r^2 l = \frac{Q}{L\rho}(1-\rho)$

$$\therefore l = \frac{Q}{\pi r^2 L \rho} (1-\rho) = \frac{10 \times (1-0.917)}{\pi \times 4 \times 10^{-4} \times 80 \times 0.917} = 9.00 \text{ cm.}$$

Example 10. The capillary tube of a Bunsen's ice calorimeter has an internal diameter of 0.4 mm. When a piece of metal of mass 0.5 gm. heated to 100°C is dropped into the calorimeter, meniscus moves 4 cm. What is the specific heat of the metal? Sp. gravity of water at $0^{\circ}\text{C}=1.00$ and that of ice $=0.917$. Latent heat of fusion of ice $=80$ cal per gm.

1 gm of water has a volume of 1.000 c.c. & 1 gm. of ice has a volume of $\frac{1}{0.917}$ c. c. or 1.091 c. c. Thus a contraction of 0.091 c. c. occurs when 1 gm of ice melts. Since the contraction $=\pi r^2 l$

$$=\pi (0.02)^2 \times 4 = 0.0016\pi.$$

\therefore Mass of ice melted $m = \frac{0.0016\pi}{0.091}$ gm.

$$\text{Heat gained by metal, } mL = \frac{0.0016\pi \times 80}{0.091}$$

$$\begin{aligned} \text{Heat lost by ice} &= MSt \\ \text{Heat lost} &= \text{Heat gained.} \end{aligned}$$

$$\therefore \frac{0.0016\pi \times 80}{0.091} = 0.5 \times S \times 100$$

$$\begin{aligned} \text{or } S &= \frac{0.0016\pi \times 80}{0.091 \times 0.5 \times 100} \\ &= 0.088 \text{ cal/gm.} \end{aligned}$$

3. Joly's Steam Calorimeter The principle involved in this method is that the heat necessary to raise a body from the room temperature to that of steam is measured by the mass of steam condensed into water at the same temperature to supply that heat.

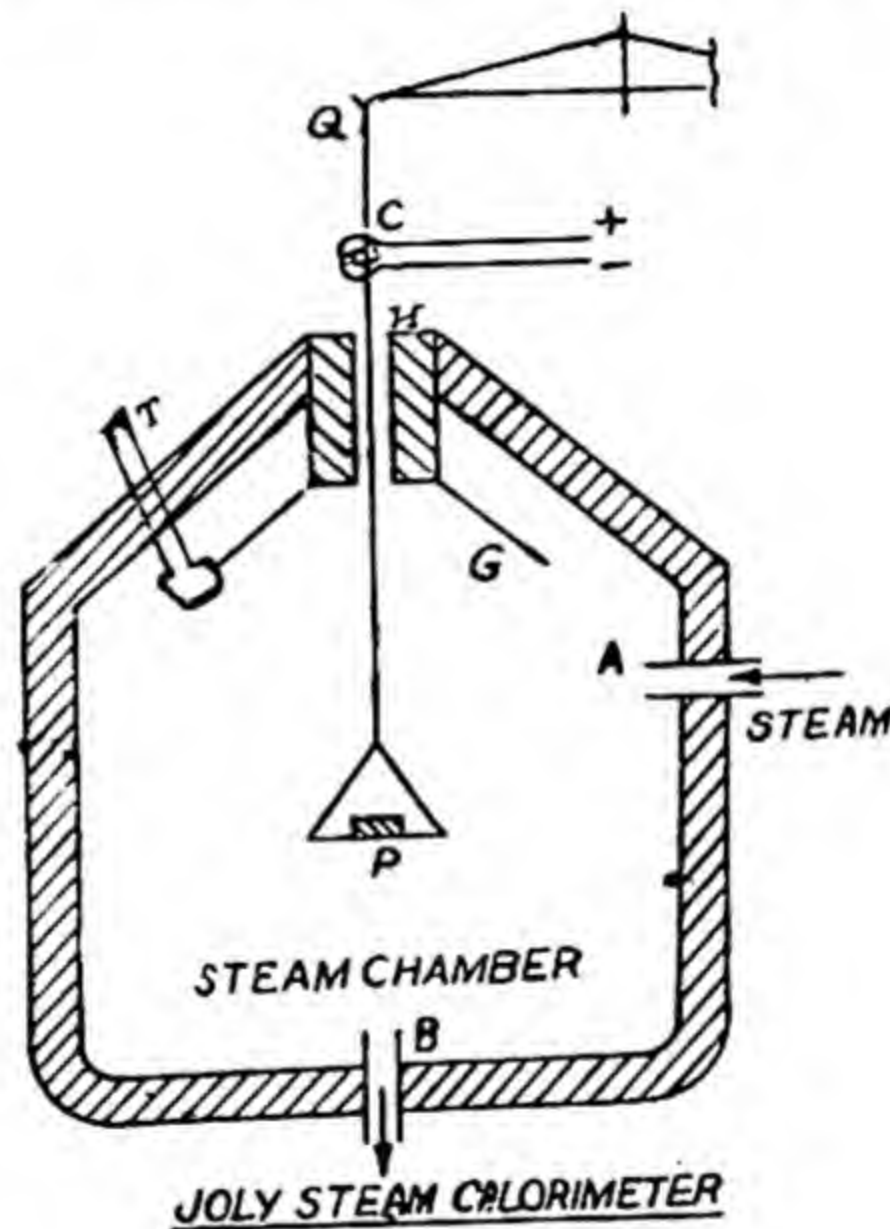


Fig.4.3.

The apparatus used is shown in Fig. 4.3. It consists of a metal steam chamber D having a thick layer of some heat-insulating material and is provided with suitable holes for letting steam in and out and for inserting thermometer T . The substance whose specific heat is required is placed in a small copper pan P suspended in a steam chamber from one arm of a delicate balance by means of a fine wire passing through a small hole H at the top of the chamber as shown. A plug of plaster of paris is fitted in H in order to prevent water of condensation from interfering with the free vertical movements of the suspension wire. Formation of water drop in H is further prevented by electrically heating the

suspension wire to the temperature of steam with the help of heating coil C immediately above the hole H . There is a shelter G provided at the top of the chamber so that steam condensed on the ceiling of the chamber may not fall on the pan P .

The mass of the substance when there is only air in the chamber is determined. The substance is then allowed to remain in the pan for some time so as to take up the temperature of the chamber and its temperature is noted with the help of thermometer T . Steam at full pressure is suddenly admitted into the chamber from tube A , which after circulating through the chamber escapes through the outlet B at the bottom. A rapid flow of steam through the chamber is necessary, essentially at the beginning, in order to prevent partial condensation of the steam due to the radiation to the cold air and walls of the chamber. Steam starts condensing on the pan P and weights are added on the other pan to maintain the balance. After five minutes or so when P ceases to increase in weight the temperature of the steam is noted. Now finally steam supply is reduced in order to avoid steam currents which would interfere with the accurate weighing. The difference between the two weights used for counterpoising at the start and end of the experiment gives the weight of the steam condensed on the pan P .

Let m = mass of solid substance in gms.

M = mass of the steam condensed on the substance and the pan in gms.

t_1 = initial temp. of solid substance i.e., of steam chamber.

t_2 = temperature of steam.

w = water equivalent of the pan etc., in gms.

S = specific heat of solid.

L = latent heat of steam in calories per gm.

Heat given out by steam during condensation on the substance and the pan = ML Cals ...(i)

Heat gained by the substance and the pan = $(mS + w)(t_2 - t_1)$...(ii)

But Heat Lost = Heat gained

Thus, we have

$$ML = (mS + w)(t_2 - t_1)$$

$$\therefore S = \frac{ML}{m(t_2 - t_1)} - \frac{w}{m}$$

Hence specific heat S can be found out.

Advantages. (1) It can be used for solids of even small mass so that specific heat of rare substances can be determined by this method.

(2) Since the final temperature of the body is the same as that of its surroundings, hence no "cooling correction" is to be applied.

(3) The only reading required in the experiment is weighing which can be done rather very accurately.

(4) It is equally applicable to powders, liquids and gases. In the case of powders and liquids, glass or metal containers are used and thermal capacity is taken into consideration. For gases a modified and improved form of the apparatus is used as will be explained in the chapter on specific heat of gases.

4. Nernst and Lindemann's Vacuum Calorimeter Method

Nernst and Lindemann have used the electrical method for measuring the specific heat of solids at **low** temperatures. Two types of calorimeters are employed (i) for good thermal conductors (ii) for bad thermal conductors. For good conducting solids, the calorimeter is made of the solid whose specific heat is to be determined. The cylindrical block of the metal *A* is drilled, and a cylindrical plug *B* of the same metal is fitted in it. *B* is shaped at the top so that good thermal contact with *A* is established. The platinum coil *H* is wound on paraffin waxed paper wrapped round the plug *B* and is kept electrically insulated from *A* by filling the inter space with paraffin wax. The platinum coil serves dual purpose.

(i) as electric heater to produce heat and

(ii) as platinum resistance thermometer for measuring the initial and final temperatures of the metal *A*.

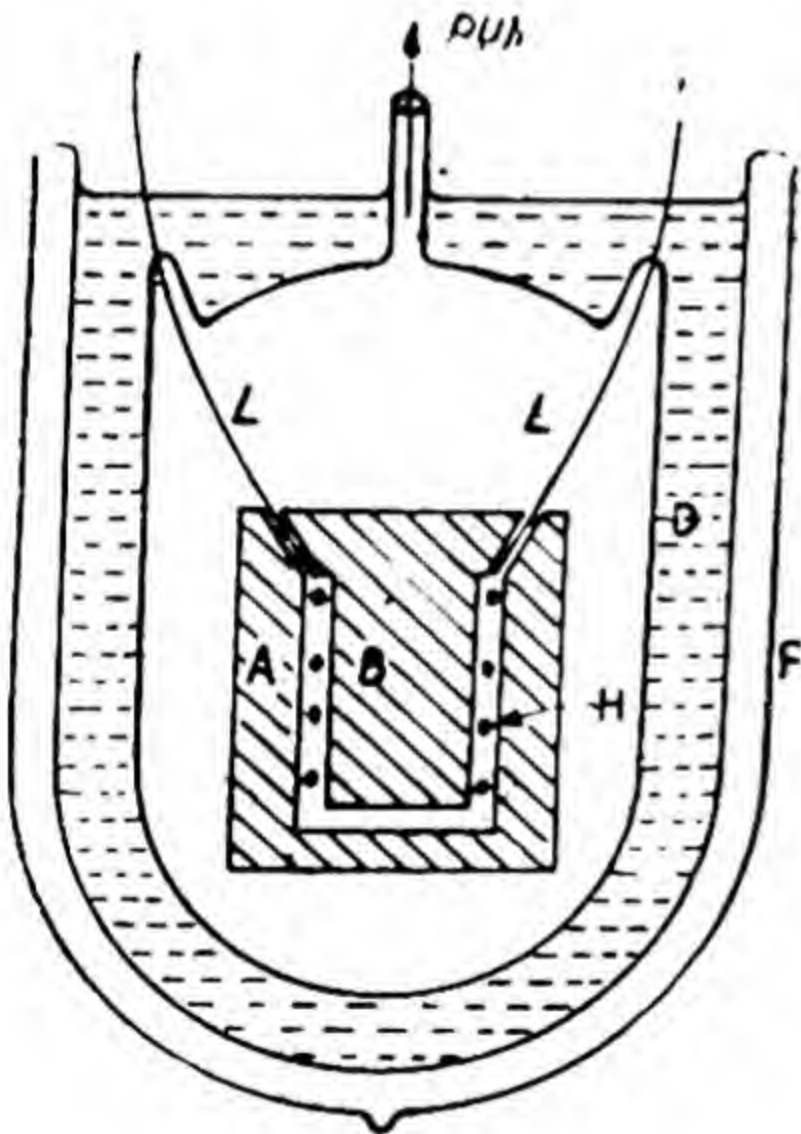


Fig. 4.4.

The whole arrangement is then suspended by the connecting leads *L* and *L'* in glass flask *D*, inside a Dewar flask *F* filled with ice or liquid air or liquid hydrogen according to the low temperature required. Hydrogen which is good conductor of heat is first admitted into *D*, and the metal eventually assumes the same temperature as the surroundings. The flask *D* is now completely evacuated and sealed, so that loss of heat by conduction or convection is almost entirely eliminated,

To determine the specific heat at a given low temperature, a current I at a known potential difference V is passed through a platinum coil for t seconds.

Let I_1 and I_2 be the initial and final values of current in amperes, then $R_1 = \frac{V}{I_1}$ and $R_2 = \frac{V}{I_2}$ the initial and final resistances of the platinum coil are readily determined. Then, applying the relation $R_2 = R_1 (1 + \alpha d\theta)$ where α is the temperature coefficient of resistance of the coil, the small rise of temperature $d\theta$ of the wire which is usually 1°C can be found out. From the average value I of the current the heat produced electrically is $\frac{VIt}{J}$ calories, where J is Joule's mechanical equivalent of heat.

Let m be the mass of the calorimeter i. e., cylinders B and A and S their specific heat, then

Heat produced electrically = Heat absorbed by the solids (B & A)
+ Heat lost by radiation.

$$\therefore \frac{VIt}{J} = mSd\theta + h$$

Neglecting the small loss of heat due to radiation, we have

$$\frac{VIt}{J} = mSd\theta$$

$$\therefore S = \frac{VIt}{Jmd\theta}$$

For solids which are bad conductors of heat, the calorimeter somewhat modified is shown in Fig 4.5. It consists of a hollow cylindrical silver vessel d on which the coil H of platinum wire is wound. The coil is covered with a layer of paraffin-waxed paper and then covered with silver foil f , soldered at the bottom to the vessel. This not only prevents the heat loss from the coil to the surroundings but also helps in distributing the heat uniformly to the vessel. The weighed amount of solid whose specific heat is to be determined is placed inside the vessel which is then closed with the lid. The silver of the vessel because of its high conductivity keeps the distribution of heat even. The tube t in the lid is closed with solder in order to prevent the air inside d from escaping. The presence of air inside the silver vessel is essential for rapidly establishing the conditions of thermal equilibrium inside the vessel. The calorimeter is then suspended by the leads LL of platinum coil in a flask D inside a Dewar flask F as before and experiment is carried as explained above for good conductors.

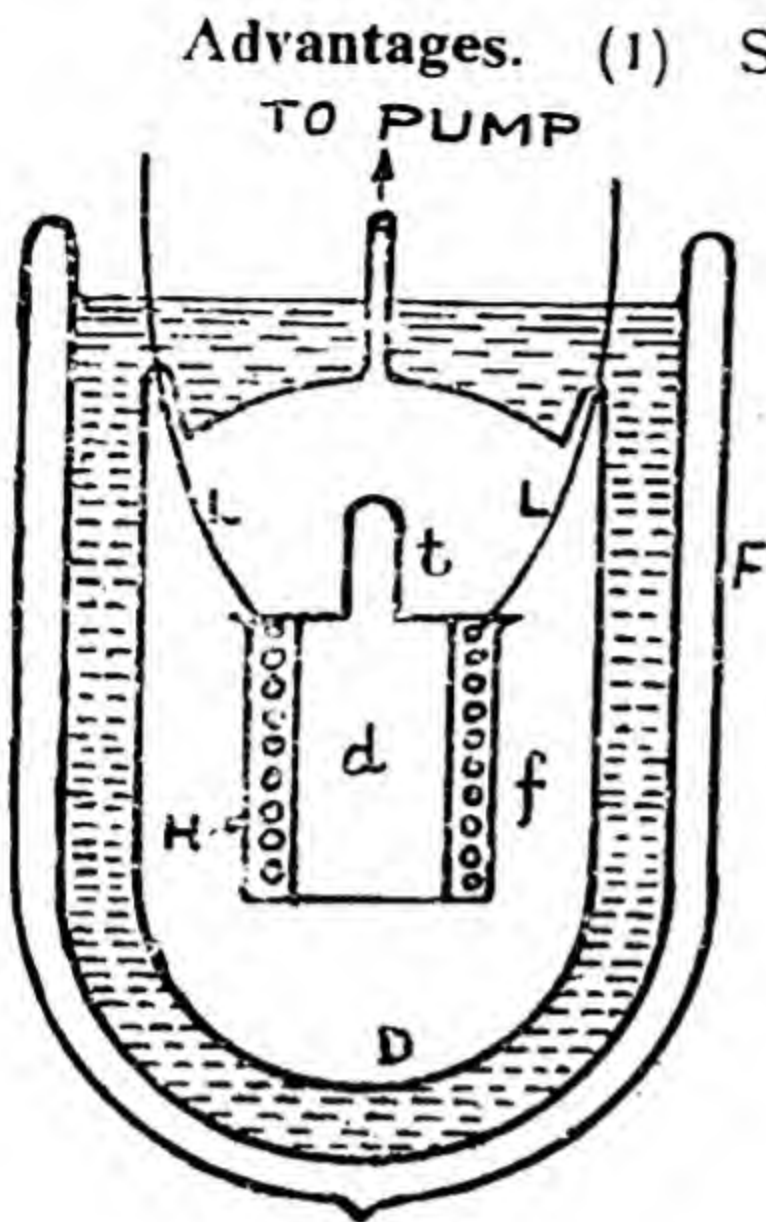


Fig. 4.5.

Advantages. (1) Since whole of the calorimeter is enclosed in vacuum the exchange of heat with the surroundings is very small.

(2) Since the rise in temperature ($d\theta$) is very small, this method gives the specific heat at a particular temperature instead of the mean value over a certain range.

It may be noted that the second type of calorimeter meant for bad conductors can be used for the determination of the specific heat of liquids and gases.

The apparatus though has been designed for low temperatures, can also be used at ordinary temperatures.

4.10. Specific Heat of Liquids. The specific heat of liquids may be found by the following methods

- (i) Method of mixtures.
- (ii) Joule's Electrical method.
- (iii) Callender and Barnes continuous flow method.
- (iv) Method of cooling.

1. Method of Mixtures. In this case the procedure is exactly the same as in Art. 4.9 except that a solid of a known specific heat is heated to a constant temperature and transferred to the calorimeter containing the liquid whose specific heat is to be determined.

If s is the specific heat of liquid, then

Heat gained by the liquid and calorimeter.

$$= (w + ms) (\theta - t)$$

and Heat lost by the solid = $MS (T - \theta)$

$$\therefore (w + ms) (\theta - t) = MS (T - \theta)$$

or Specific heat of liquid.

$$s = \frac{MS (T - \theta)}{m (\theta - t)} - \frac{w}{m}$$

Where M = mass of the hot solid

S = Specific heat of solid.

T = The temperature of the hot solid.

t = Initial temperature of the liquid.

θ = Final temperature of the mixture

w = water equivalent of the calorimeter = $m_1 s$.

where m_1 = mass of the calorimeter.

Example 11. 200 gm. of water at 98°C were mixed with 200 c.c. of milk of density 1.03 at 30°C contained in a brass vessel of thermal capacity equal to that of 8 gm. of water and the temperature of the mixture was 64°C . Find the specific heat of milk.

(A. M. I.E.)

$$\begin{aligned}
 \text{Mass of water} &= 200 \text{ gm.} \\
 \text{Fall in temperature} &= (98 - 64) = 34^{\circ}\text{C} \\
 \text{Heat lost by water} &= 200 \times 1 \times 34 = 6800 \text{ cal.} \\
 \text{Mass of milk} &= 200 \times 1.03 = 206 \text{ gms.} \\
 \text{Rise in temperature} &= (64 - 30) = 34^{\circ}\text{C.} \\
 \text{Heat gained by milk} &= 206 \times S \times 34 \\
 &\text{where } S \text{ is the specific heat of milk.} \\
 \text{Water equivalent of brass vessel} &= 8 \text{ gm.} \\
 \text{Heat gained by brass vessel} &= 8 \times 34 = 272 \text{ cal.} \\
 \text{Total Heat gained} &= (206 \times S \times 34 + 272) \text{ cal.} \\
 \text{Heat lost} &= \text{Heat gained} \\
 \therefore 6800 &= (206 \times S \times 34 + 272) \\
 \text{or } S &= \frac{6800 - 272}{206 \times 34} = 0.932 \text{ cal/gm}
 \end{aligned}$$

2. Joule's Electrical Method. This is a laboratory method and employs electrical heating. The apparatus consists of a heating coil H suspended in a copper calorimeter covered with an ebonite disc. The ends of the coil are soldered to copper leads which are further connected to two binding screws S_1 and S_2 fixed on the top of the lid as shown. The lid has two holes, through one passes a sensitive thermometer and through the other a stirrer. The calorimeter is placed in an outer jacket which is packed with cotton wool to minimise loss of heat by conduction and radiation. The terminals S_1 and S_2 are connected to a rheostat R , ammeter A , battery B and key K in series. A voltmeter V is connected in parallel with the terminals S_1 and S_2 as shown.

First of all the weight of the calorimeter and the stirrer with lid is taken. Now, the calorimeter is filled nearly half with the liquid whose specific heat is required. It is weighed again to find out the weight of the liquid. The lid is placed with the coil H in position so that the coil is immersed in the liquid without touching the sides of the calorimeter. The liquid is kept stirred by a suitable stirrer.

After closing the circuit, current I and potential difference V are adjusted in such a way that rise in temperature is about $\frac{1}{2}^{\circ}\text{C}$ in one minute. Key is taken out and after stirring the liquid well, its initial temperature is noted very accurately. The key is inserted and a constant current of I amperes is made to

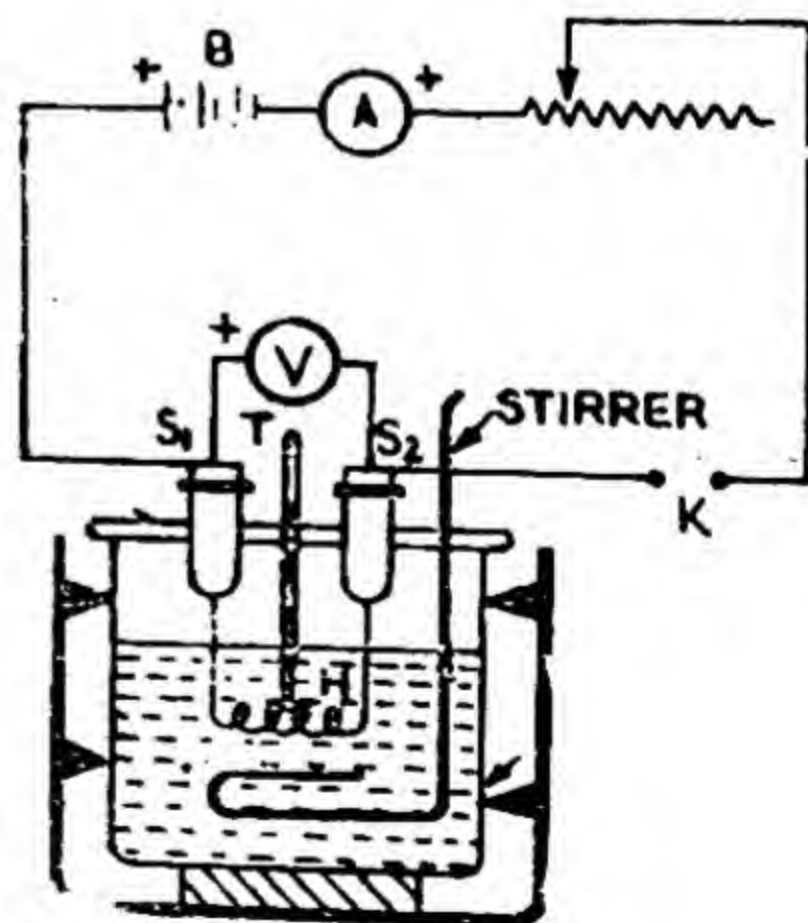


Fig. 4.6.

pass through the coil for the time the rise of temperature of the liquid of about 10°C is obtained. The readings of ammeter and voltmeter are noted. The time in which this rise of temperature has occurred is noted with the help of stop watch.

Let m = mass of the liquid

S = specific heat of the liquid

w = water equivalent of the calorimeter

t_1 = initial temperature of the liquid

t_2 = final temperature of the liquid

V = potential difference across the coil (reading of voltmeter V)

I = current through the heating coil (reading of ammeter)

t = the time for which current passes.

Heat produced electrically = $\frac{VIt}{J}$ calories.

where J is the mechanical equivalent of heat = 4.2 joules/cal.

Heat gained by the liquid and calorimeter = $(w + mS)(t_2 - t_1)$

If h is the heat loss from the calorimeter, then

$$\frac{VIt}{J} = (w + mS)(t_2 - t_1) + h$$

If the rise of temperature is small, the loss of heat due to radiation is negligible. Hence neglecting the loss of heat due to radiation, we have,

$$\frac{VIt}{J} = (w + mS)(t_2 - t_1)$$

or
$$S = \frac{VIt}{mJt} - \frac{w}{m}$$

where $t_2 - t_1 = t$ (rise of temperature)

3. Callender and Barne's Continuous flow method. It is based on the same principle as joule's method. The apparatus consists of a heating coil of fine platinum wire H in the form of a spiral. The spiral form of coil helps in two ways (i) It increases surface area exposed to the liquid. (ii) It helps in thorough stirring of liquid as it flows. The platinum resistance wire is mounted in a narrow glass or quartz tube T (2 m.m. in diameter) with its ends fixed to two thick copper tubes C_1C_2 . The liquid whose specific heat is required is made to flow continuously through the tube T at a steady rate and is heated by passing a current through platinum resistance wire by means of battery circuit connected to the copper tubes as shown in Fig. 4.7. In each copper tube is inserted a bulb of platinum resistance thermometers P_1, P_2 to measure the temperature of the liquid on entering and on leaving the tube. The copper tubes serve two

important purposes (i) due to their high conductivity, they keep the whole bulb at the temperature of the surrounding

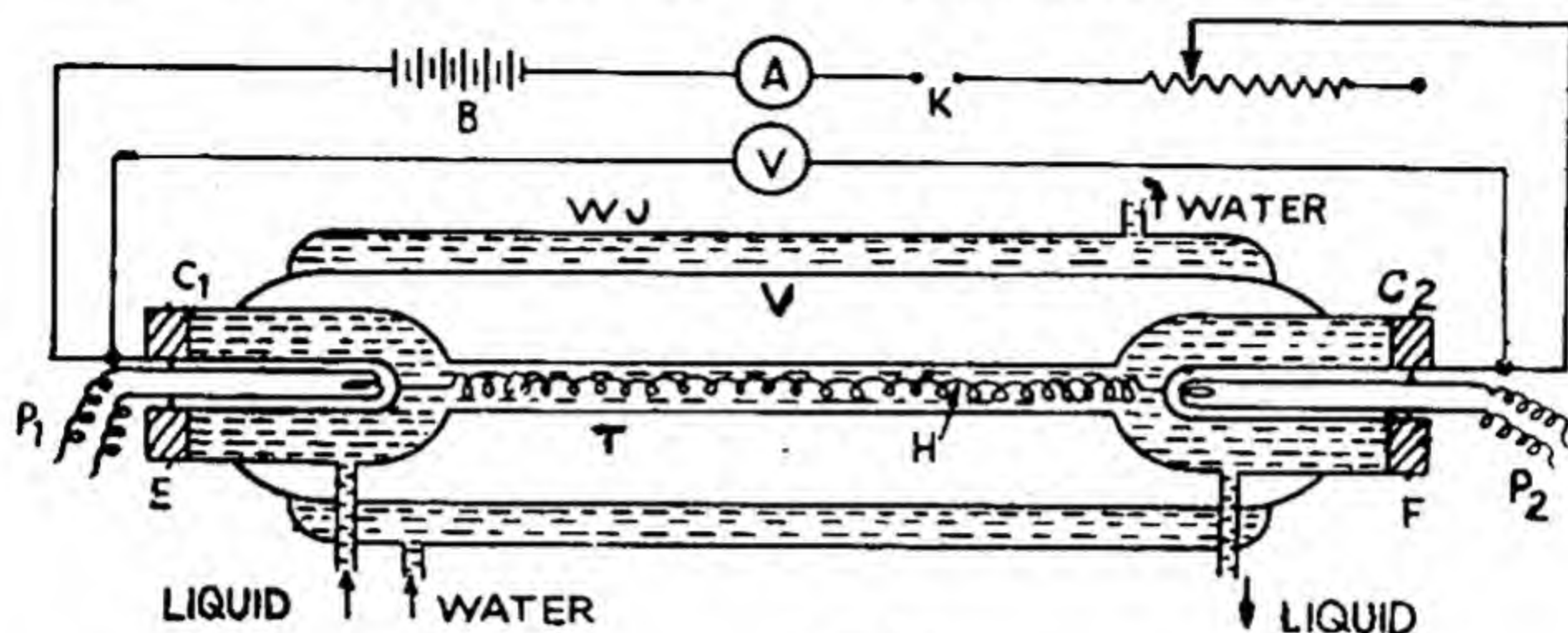


Fig. 4.7

liquid and (ii) due to their low resistance, they do not let an appreciable amount of heat to be produced near the bulbs of the thermometers. The tube T has two openings, one for allowing the liquid to flow into the tube and other for allowing it to go out of it after being heated. This tube is enclosed in a vacuum jacket V which is further surrounded by another jacket through which water is continuously circulated. This arrangement is made to minimise loss of heat due to conduction and radiation. The tube is closed on both sides by non-conducting lids E and F . To corresponding ends of both the copper tubes are connected battery B , rheostat R , ammeter A and key K . The voltmeter is connected in parallel with the spiral.

The liquid whose specific heat is to be determined is made to flow through the tube T at a constant rate. The key K is inserted so as to close the circuit. The electric current now flows through the platinum spiral & thus the liquid is heated on its passage through the tube. Sufficient time is allowed for the apparatus to settle down to a steady state in which case all the heat produced electrically is carried away by the liquid and none is used up by the apparatus to raise the temperature of any of its parts. When a steady state is reached as indicated by the constancy in the readings of the thermometers P_1, P_2 then the mass of the liquid flowing for t seconds is found.

- Let
- m = mass of the liquid flowing in t seconds
 - t_1 = Temperature of the entering liquid as indicated by thermometer P_1 .
 - t_2 = Temperature of the leaving liquid as indicated by thermometer P_2 .
 - S = Specific heat of the liquid
 - V = Voltmeter reading in volts
 - I = Ammeter reading in amperes

Heat gained by liquid = $mS(t_2 - t_1)$

Heat produced by current in time t seconds

$$= \frac{VIt}{J} \text{ calories}$$

If h is the loss of heat due to radiation, then

$$\frac{VIt}{J} = mS(t_2 - t_1) + h \quad (i)$$

To eliminate the radiation loss, the experiment is repeated with voltage V' , current I' and a different mass m' of the liquid for the same time t , over the same temperature range $(t_2 - t_1)$, then

$$\frac{V'I't}{J} = m'S(t_2 - t_1) + h \quad (ii)$$

Subtracting (i) from (ii) we have

$$\frac{(V'I' - VI)t}{J} = (m' - m)S(\theta_2 - \theta_1)$$

$$\text{or } S = \frac{(V'I' - VI)t}{J(m' - m)(\theta_2 - \theta_1)}$$

Advantages (i) Since the flow is steady there is no change of temperature in any part of the apparatus during the experiment and hence no correction is required for the thermal capacity of the calorimeter.

(ii) The temperature of the inflowing liquid can be measured more accurately by using platinum resistance thermometers which would have been otherwise useless if changing temperatures were to be measured.

(iii) Radiation losses are almost eliminated.

(iv) By choosing suitable values of V and I , the rise in temperature can be made small so that specific heat of liquid at any temperature can be found out.

(v) This method can be used for investigating variation of specific heat of water with temperature. Callender and Barne's also used this method for finding the specific heat of mercury, the spiral coil in this case was dispensed with as the continuously flowing mercury served as the conductor.

(vi) This method is used for the determination of Joule's mechanical equivalent of heat.

Example 12. It is observed that the temperature of 300 gms. of a liquid in a vacuum flask of water equivalent 20 gms, rises by 180°C when a current of 1.8 amp. passes through the heating coil of 10 ohms resistance in the liquid for one hour. Find the specific heat of the liquid if $J = 4.18 \text{ joules/cal.}$

Mass of the liquid	$m = 300 \text{ gms.}$
Water equivalent of the flask	$w = 20 \text{ gms.}$
Rise in temp.	$(t_2 - t_1) = 180^\circ\text{C}$
Resistance of heating coil	$R = 10 \text{ ohms.}$
Current passing	$I = 1.8 \text{ Amp.}$

Time

$$t = 1 \text{ hour} = 3600 \text{ seconds.}$$

Specific heat

$$S = \frac{VIt}{mJ(t_2 - t_1)} = \frac{w}{m}$$

But

$$V = IR$$

 \therefore

$$S = \frac{I^2 R t}{mJ(t_2 - t_1)} = \frac{w}{m}$$

Substituting the values, we have

$$\begin{aligned} \therefore S &= \frac{(1.8)^2 \times 10 \times 3600}{300 \times 180 \times 4.18} = \frac{20}{300} \\ &= 0.517 - 0.067 = 0.45 \end{aligned}$$

Example 13. In a continuous flow experiment, liquid passing at a rate of 10 gm/mt. over heating coil is heated from 22°C to 32°C when the potential difference between the ends of the coil is 3 volts and current is 1.5 A, when the rate of flow is changed to 4 gm/mt. the same rise of temperature occurs for a potential difference of 1.5 volts and a current of 1.44 A.

Calculate (i) the specific heat of the liquid and (ii) the rate at which heat is lost from the surface of the tube carrying the liquid. Take $J = 4.18$ joules/cal.

For the first observation,

$$\frac{VIt}{J} = (w + mS)(t_2 - t_1) + h \quad \dots(i)$$

where h is heat loss due to radiation

For the second observation,

$$\frac{V'I't}{J} = (w + m'S)(t_2 - t_1) + h \quad \dots(ii)$$

From (i) and (ii) we have

$$\begin{aligned} S &= \frac{(V'I' - VI)t}{J(m' - m)\theta} \text{ where } \theta = t_2 - t_1 = \text{rise of temp.} \\ &= \frac{(3 \times 1.5 - 1.5 \times 1.4)1}{4.18 (10/60 - 4/60) \times 10} = 0.575 \text{ cal/gm/}^\circ\text{C.} \end{aligned}$$

Substituting this value of S in equation (i) we have

$$\frac{3 \times 1.5}{4.18} = \left(0 + \frac{10}{60} \times 0.575\right)(10) + h.$$

$$\text{or } h = \frac{3 \times 1.5}{4.18} - \frac{100}{60} \times 0.575 = 0.125 \text{ cal/sec.}$$

Example 14. In an experiment with Callender and Barne's continuous flow method the potential difference across the wire was 2.5 volts and current flowing was 2 amps. The rise in temperature of the liquid is 5°C when the rate of flow is 32 gms. per mt. The rate of flow was then increased to 50 gms. per mt., the potential difference to 3 volts and the current to 2.5 amps. the temperature difference being the same as before. Calculate the specific heat of the liquid, given $J = 4.2$ joules/cal.

First Case.

Temperature difference $t_2 - t_1 = 5^\circ\text{C}$

Mass of liquid flowing per mt. $m = 32$ gms.

Current flowing $I = 2.0$ amp.

Potential difference $V = 2.5$ volts.

2nd. Case.

Mass of liquid flowing per mt. $m' = 50$ gms.

Current flowing $I' = 2.5$ gms.

Potential difference $V' = 3.0$ volts.

As the rise of temperature in the two cases is the same,

$$\begin{aligned} \therefore S &= \frac{(V'I' - VI)t}{(m - m')J(\theta_2 - \theta_1)} \\ &= \frac{(3 \times 2.5 - 2.5 \times 2) 60}{(50 - 32) \times 5 \times 4.2} = 0.4 \text{ gm/cal/}^\circ\text{C} \end{aligned}$$

4. Method of cooling. This method makes use of Newton's law of cooling. We shall therefore, first make a detailed study of this law.

Newton's Law of cooling. When a hot cup of tea is placed for some time it becomes cold because it loses heat and air surrounding it gains heat. At first it loses heat quickly but later on the loss of heat becomes slow. Newton put forward a law regarding the rate of loss of heat and it is called Newton's Law of cooling.

Newton's Law of cooling. It states that the rate at which a body loses heat is directly proportional to the temperature difference between the body and that of the surroundings. The amount of heat radiated depends upon the extent and nature of the radiating surface.

Let θ be the temperature of the body at any instant, and θ_0 the temperature of the surroundings. Then, according to Newton's Law of cooling, the heat loss is proportional to the temperature difference $(\theta - \theta_0)$. It follows that the rate of fall of temperature will also be proportional to $(\theta - \theta_0)$

$$\text{Hence } -\frac{dQ}{dt} \propto (\theta - \theta_0)$$

$$\text{or } -\frac{dQ}{dt} = k(\theta - \theta_0)$$

Where dQ is the amount of heat lost in time dt and k is a constant, depending upon the area and nature of the surface. The negative sign shows that the temperature falls as time lapses.

The experiments have revealed that if the body is surrounded by still air the law holds good for small differences of temperatures up to about 30°C . But under ventilated cooling in draught i.e., under forced convection, the law is true even if the temperature difference is large.

If m is the mass and S the specific heat and $d\theta$ is the fall of temperature in the time dt , then

$$dQ = m s d\theta$$

$$\therefore -mS \cdot \frac{d\theta}{dt} = k(\theta - \theta_0)$$

$$\text{or} \quad \frac{d\theta}{dt} = -\frac{k}{mS}(\theta - \theta_0)$$

$$= -K(\theta - \theta_0)$$

where K is another constant and is equal to $\frac{k}{mS}$

$$\text{or} \quad \frac{d\theta}{\theta - \theta_0} = -K dt$$

$$\text{or} \quad \int \frac{d\theta}{\theta - \theta_0} = -K \int dt$$

$$\text{or} \quad \log(\theta - \theta_0) = -Kt + C.$$

where C is a constant of integration. This equation is of the

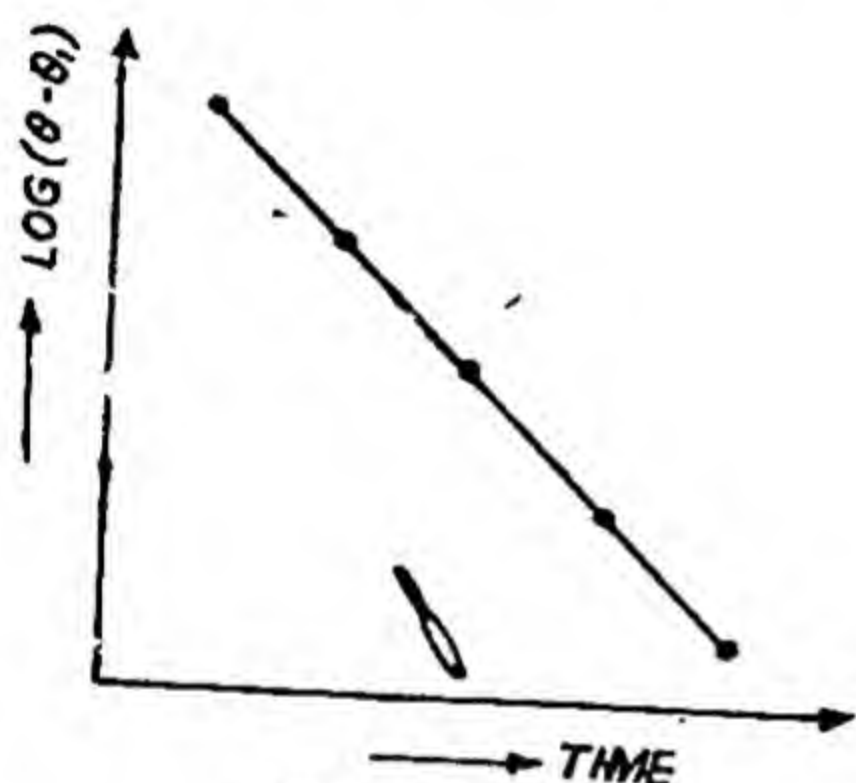


Fig. 4.8.

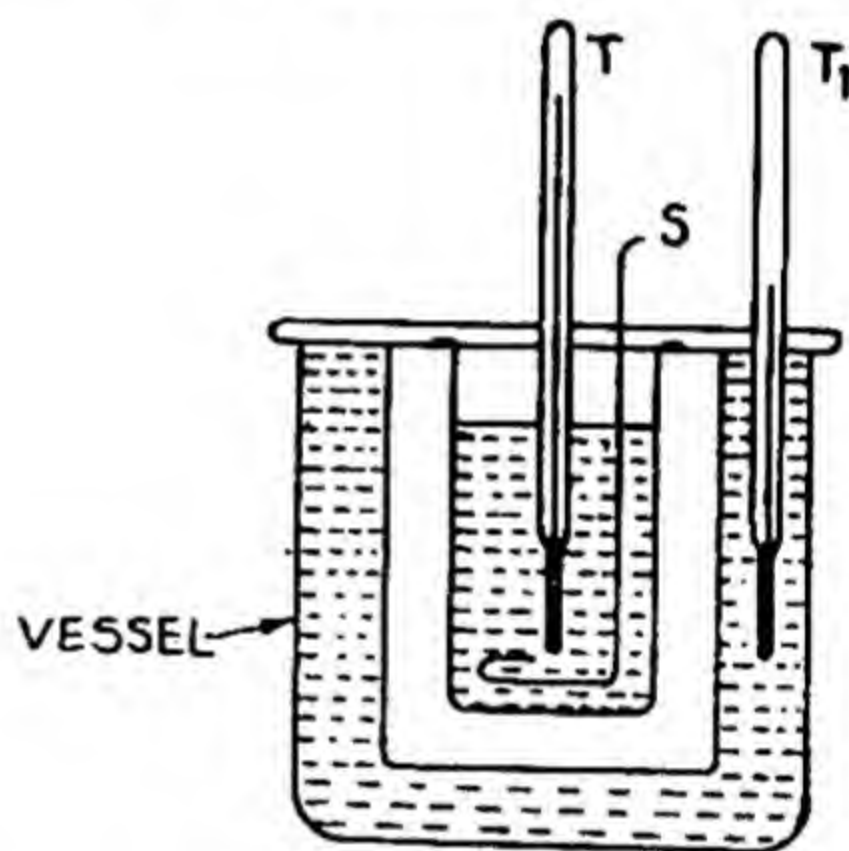


Fig. 4.9.

form $y = mx + c$. Hence the graph between $\log(\theta - \theta_0)$ and time t will be a straight line as shown in Fig. 4.8.

Newton's law of cooling can be verified by the following experiment.

A calorimeter blackened from outside is taken and is filled up to nearly $\frac{3}{4}$ th with the hot water at a temperature about 80°C . The calorimeter is suspended in a double-walled vessel as shown in Fig. 4.9. This vessel contains water and has a thermometer immersed in it to find temperature of the surroundings. The water in the calorimeter is kept stirred and allowed to cool. The temperature is noted after an interval of $\frac{1}{2}$ a minute till the temperature of water approaches the room temperature. The difference of temperature is found at different intervals of time and a graph is plotted between $\log(\theta - \theta_0)$ and time. It is found to be a straight line and hence Newton's law of cooling is verified.

Limitations. (i) This law is applicable only if temperature of the whole body is kept uniform by stirring it. Hence it is applicable to liquids only.

(ii) The cooling body should be exposed to draughts by placing it in open window or under a fan.

(iii) If a body cools in still air by convection only, then this law is true upto 30°C difference of temperature.

Specific heat of liquid by the method of cooling. If a liquid, heated to a temperature above its surroundings, is put in a calorimeter and allowed to cool in an enclosure, then the rate of cooling depends upon the following factors.

(i) the temperature difference between the body and the surroundings.

(ii) the area of the radiating surface.

(iii) the nature of the radiating surface.

It should be noted that the rate of cooling does not depend upon the nature of the liquid. Thus if the above factors are made exactly the same for two different liquids, their rates of cooling must be the same. This is the principle of the cooling method employed for the determination of specific heat of a liquid as given below.

Two exactly similar, small copper calorimeters blackened from

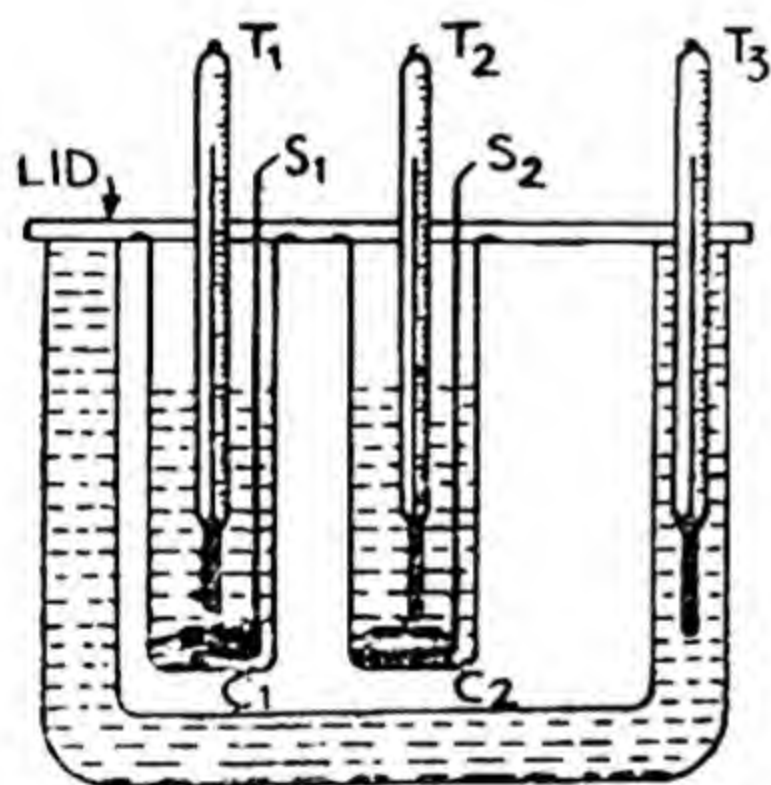


Fig. 4.10.

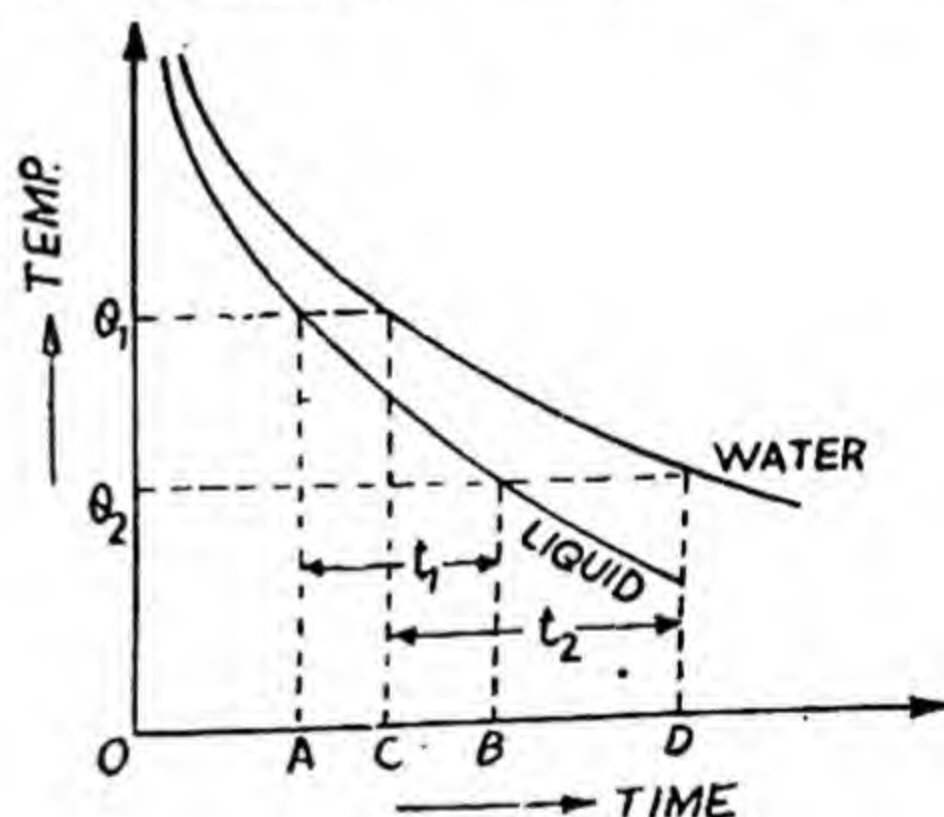


Fig. 4.11.

outside and having the same thermal capacities are taken. A double walled vessel with water between the walls is used as a constant temperature enclosure. The calorimeters when empty are weighed and are afterwards suspended inside the enclosure as shown in Fig. 4.10. Now water and given liquid whose specific heat is to be determined are heated to a temperature of about 30°C to 35°C above the room temperature. Equal volumes of the two are then put in the calorimeters. The calorimeters and the enclosure are covered by a lid provided with small holes to insert the thermometers T_1 , T_2 and T_3 and stirrers inside the calorimeters. The water and the liquid are kept stirred continuously and the temperature of each after every half minute interval is recorded. At the end of the observations, the two calorimeters are weighed again and the mass of water and that of the same volume of the liquid are found out. The cooling curves are then plotted between the time and the temperature in each case as shown in Fig. 4.11. The time taken by the

liquid and the water in falling through a certain range of temperature θ_1 (about 35°C) and θ_2 (30°C) are found from the curves. Let these times be t_1 and t_2 respectively and

m_1 = mass of liquid

m_2 = mass of water

w = water equivalent of each calorimeter

S = specific heat of liquid

Total heat lost by the liquid and the calorimeter

$$= m_1 S (\theta_1 - \theta_2) + w (\theta_1 - \theta_2)$$

$$= (m_1 S + w) (\theta_1 - \theta_2)$$

Rate of loss of heat of the liquid

$$= \frac{(m_1 S + w) (\theta_1 - \theta_2)}{t_1}$$

...(i)

Total heat lost by water and the calorimeter

$$= m_2 \times 1 \times (\theta_1 - \theta_2) + w (\theta_1 - \theta_2)$$

$$= (m_2 + w) (\theta_1 - \theta_2)$$

Rate of loss of heat of water

$$= \frac{(m_2 + w) (\theta_1 - \theta_2)}{t_2}$$

...(ii)

Since the rates of cooling are equal we have

$$\frac{(m_1 S + w) (\theta_1 - \theta_2)}{t_1} = \frac{(m_2 + w) (\theta_1 - \theta_2)}{t_2}$$

or $(m_1 S + w) = (m_2 + w) \frac{t_1}{t_2}$

or $S = \frac{(m_2 + w)t_1}{m_1 t_2} - \frac{w}{m_1}$

Other quantities being known, S the specific heat of the liquid can be found out from the above expression.

Note. It should be noted that the rates of loss of heat are equal and not the rates of fall of temperature.

The **advantage** of this method is that the liquid has not to be mixed with water, and hence no heat due to chemical action is either evolved or absorbed. The **disadvantage** of this method is that both the liquids cannot be cooled under **identical** conditions. A slight variation in the conditions has a large effect on the accuracy of the result.

Example. 15. 250 gms. of water and an equal volume of alcohol of mass 200 gms. are placed successively in the same calorimeter and cooled from 60°C to 55°C in 130 seconds and 67 seconds respectively. Find the specific heat of alcohol. The water equivalent of calorimeter is 10 gms. (P.U.)

Water equivalent of calorimeter	$w = 10$ gms.
Mass of water	$m_2 = 250$ gms.
Mass of same volume of alcohol	$m_1 = 200$ gms.
Fall in temperature	$(\theta_2 - \theta_1) = (60 - 55) = 5^{\circ}\text{C}$.
Time taken by water to fall through	$5^{\circ}\text{C}, t_2 = 130$ seconds.
Time taken by alcohol to fall through	$5^{\circ}\text{C}, t_1 = 67$ seconds.

Let the specific heat of alcohol be S , then

$$\begin{aligned}
 S &= \frac{(m_2 + w) t_1}{m_1 t_2} - \frac{w}{m_1} \\
 &= \frac{(250 + 10) 67}{200 \times 130} - \frac{10}{200} \\
 &= 0.67 - 0.05 = 0.62
 \end{aligned}$$

Example 16. 80 c.c. of water contained in the calorimeter weigh 150 gms. and of specific heat 0.1 takes 12 minutes to cool from 40°C to 15°C . Same volume of alcohol of density 0.8 gm./c.c. using the same calorimeter takes 8 minutes to cool from 40°C to 15°C . Calculate the specific heat of alcohol. Density of water = 1 gm./c.c.

Volume of the alcohol	$= 80$ c.c.
Density of alcohol	$= 0.8$ gm./c.c.
Mass of the alcohol	$m_1 = 80 \times 0.8 = 64$ gms.
Volume of water	$= 80$ c.c.
Density of water	$= 1$ gm./c.c.
Mass of water	$m_2 = 80 \times 1 = 80$ gms.
Time taken by alcohol to fall from 40°C	
to $15^{\circ}\text{C}, t_1 = 8 \times 60 = 480$ secs.	
Time taken by water to fall from 40°C	
to $15^{\circ}\text{C}, t_2 = 12 \times 60 = 720$ secs.	
Mass of the calorimeter	$= 150$ gms.
Specific heat of the material of the calorimeter	$= 0.1$

\therefore water equivalent of the calorimeter $w = 150 \times 0.1 = 15$ gms.

Hence
$$S = \frac{(m_2 + w) t_1}{m_1 t_2} - \frac{w}{m_1}$$

$$= \frac{(80 + 15) 480}{64 \times 720} - \frac{15}{64} = 0.755$$

Expected Questions

1. (a) Define Calorie, C.H. U. and B.Th. U. and derive the relation between them. (A.M.I.E.)
 (b) Define specific heat and thermal capacity. How does specific heat differ from thermal capacity?
2. How can the specific heat of a solid be determined? Describe an experiment to determine the specific heat of a solid. Mention the various sources of error and how are they avoided. (A.M.I.E.)
3. Describe Bunsen's Ice calorimeter, how would you use it to determine the specific heat of a metal or liquid available in a small quantity. (A.M.I.E.)
4. Describe an accurate electrical method for finding out the specific heat of a solid at low temperatures.
5. Describe a simple laboratory method to find the specific heat of a liquid.
6. State Newton's Law of cooling, pointing out the conditions under which it is likely to hold. Give the method of determining the specific heat of a liquid by this method. (A.M.I.E.)
7. (a) Describe the continuous flow method of measuring the specific heat of a liquid.
 (b) What are the (i) advantages and (ii) the difficulties of the continuous flow method. How is radiation loss eliminated in this method?

CHAPTER V

SPECIFIC HEAT OF GASES

5.1. Two specific heats. While defining specific heat of a solid or a liquid it was assumed that whole of the heat acquired by a substance is used for raising its temperature only.

If the specific heat is defined merely as the quantity of heat required to raise unit mass through 1°C , then its value will depend not only on the nature of the substance, but also on the amount of external work done due to the expansion of the substance caused by the rise in temperature. In the case of solids and liquids this change of volume is very small and hence the external work done during the change in temperature is negligible but in the case of gases large changes occur both in pressure as well as in volume. For this reason the external conditions under which the heating of a gas takes place are important and must be stated when specific heat is to be determined. Generally all measurements of heat for solids and liquids are made by heating the substance at constant pressure. So specific heat of solids and liquids is always found at constant pressure. But a gas can have any value of specific heat lying between zero and infinity depending upon the manner in which it is being heated.

Thus when a gas is heated, ordinarily there is an increase in volume as well as pressure in addition to the rise of temperature. For the sake of simplicity either the volume or the pressure may be kept constant. Therefore, a gas has two specific heats :—

(i) Specific heat at constant volume (C_v) i.e., when the gas is heated at constant volume.

(ii) The specific heat at constant pressure (C_p) i.e., when the gas is heated at constant pressure.

These two specific heats are called the principal specific heats of a gas.

5.2. Specific heat of a gas at constant volume. *It is the amount of heat required to raise the temperature of one gm. of a gas through 1°C when its volume is kept constant. It is denoted by c_v .*

Let 1 gm. of a gas be enclosed in an air-tight container of capacity V c.c. When the enclosed gas is heated, its temperature goes on increasing resulting in an increase of its pressure at constant volume. Whole of the heat absorbed by the gas is used in raising the temperature. Let 1 gm. of enclosed gas require q units of heat for raising its temperature through 1°C .

$$\begin{aligned}\text{then } q &= \text{mass} \times \text{sp. heat at constant volume} \times \text{rise in temp.} \\ &= 1 \times c_v \times 1 = c_v\end{aligned}$$

Hence for m gm. of gas and for temperature rise of $d\theta = (\theta_2 - \theta_1)$, the total quantity of heat Q is

$$\begin{aligned}Q &= mc_v (\theta_2 - \theta_1) \\ &= mc_v d\theta\end{aligned}\tag{i}$$

5.3. Specific heat of a gas at constant pressure. *It is the amount of heat required to raise the temperature of one gram of a gas through 1°C when its pressure is kept constant. It is denoted by c_p .*

Let 1 gm. of the same gas be enclosed in a cylinder fitted with frictionless movable piston. On heating, the enclosed gas expands thus pushing the piston upwards against external or atmospheric pressure which remains constant. For pushing the piston upwards some energy is required.

Let q' be the amount of heat required by 1 gm. of enclosed gas for heating it through 1°C at constant pressure, then

$$q' = 1 \times c_p \times 1 = c_p \quad \dots(ii)$$

This amount of heat is utilised for the following two purposes :—

(i) *For raising the temperature of the enclosed gas through 1°C .* This heat q units remains within the body of the gas and is the same as explained in relation (i).

(ii) *For doing the external work.* Some heat energy of q_1 units is required for enabling the gas to expand against external pressure.

$$\therefore q' = q + q_1$$

If P is the external pressure and dV the increase in volume then,

$$q_1 = \frac{PdV}{J}$$

= thermal equivalent of work done.

$$\text{or } 1 \times c_p \times 1 = 1 \times c_v \times 1 + q_1$$

$$\text{or } c_p = c_v + \frac{PdV}{J}$$

Thus the specific heat at constant pressure is always greater than the specific heat at constant volume by the thermal equivalent of work done $\frac{PdV}{J}$ against external pressure.

If m gm. of the gas are heated from $\theta_1^\circ\text{C}$ to $\theta_2^\circ\text{C}$ under constant pressure then total heat taken is $mc_p (\theta_2 - \theta_1)$ or $mc_p d\theta$. It has been explained above that during heating at constant pressure, extra work has to be done.

In general we define specific heat corresponding to gram molecule of a gas and not a unit mass of it. Such specific heats are called **gram-molecular** or **molar specific heats**. The gram-molecular specific heat at a constant pressure is denoted by C_p and gram molecular specific heat at constant volume by C_v . If M is the molecular wt. of the gas then

$$C_p = Mc_p$$

and

$$C_v = Mc_v$$

Hence when heat energy is supplied to a gas, in general part of it is used in doing some external work and the rest remains within the body of the gas for raising its temperature. The first part for doing external work represents the **External energy** of the gas and the second part which is utilized for raising the temperature is known as the **Internal energy** of the gas. The symbol for internal energy is E .

5.4. Relation between two specific heats. Consider unit mass (gm or kg.) of a gas enclosed in a cylinder fitted with a frictionless movable piston, at a pressure P and absolute temperature T_1 . Let it be heated and the temperature of the gas rises from T_1^0 to T_2^0 absolute.

If the volume is kept constant by increasing the pressure, then whole of heat is utilized to increase the internal energy of the gas.

The heat required to raise the temperature by $(T_2 - T_1) = dT$ at constant volume is given by

$$q = 1 \times C_v dT = C_v dT$$

If instead of the volume, the pressure is kept constant and the volume is allowed to increase, then an additional amount of heat equivalent to the work done by the gas is also required. This work done is calculated as follows.

Let A be the area of the piston which moves outwards by distance dx due to the expansion of the gas, then

The force on the piston $= P \times A$

Work done by the gas in expanding against the external pressure

$$= \text{Force} \times \text{distance moved}$$

$$= P \times A \times dx$$

$$= PdV$$

where dV is equal to the increase in volume. $= A \times dx$

Additional amount of heat required $= \frac{PdV}{J}$

where J is the Mechanical equivalent of heat.

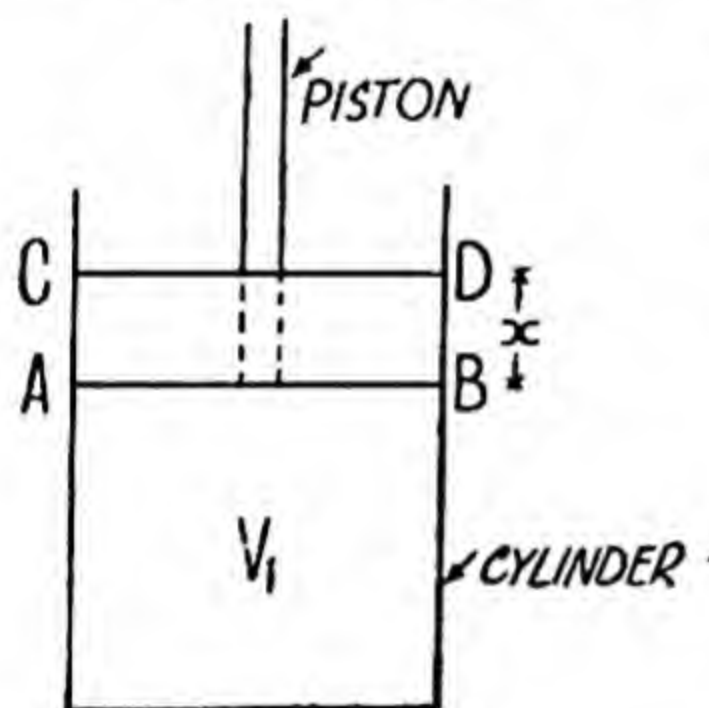


Fig. 5.1.

If C_p is the specific heat at constant pressure, then total heat required to raise the temperature through dT is equal to $C_p dT$

Hence

$$q' = q + q_1$$

\therefore

$$C_p dT = C_v dT + \frac{PdV}{J}$$

or

$$(C_p - C_v) dT = \frac{PdV}{J} \quad (i)$$

But for a perfect gas $PV = RT$

Differentiating we get (pressure P and R are constant)

$$PdV = RdT$$

Substituting this value in equation (i) we have

$$(C_p - C_v) dT = \frac{RdT}{J}$$

or

$$(C_p - C_v) = \frac{R}{J}$$

If the gas constant R is expressed in heat units then the equation

$(C_p - C_v) = \frac{R}{J}$ can be written as

$$C_p - C_v = R$$

This result is important since it proves that the *characteristic* constant R of a gas is equal to the difference between its two principal specific heats.

When unit of mass is 1 gm., unit of work is erg, unit of heat is calorie

then

$$C_p - C_v = \frac{R}{J} \text{ cal/gm/}^\circ K.$$

when unit of mass is 1 Kgm, unit of work is joule and unit of heat is Kilo-cal.

then

$$C_p - C_v = \frac{R}{J} \text{ Kilo-cal./Kg/}^\circ K.$$

If C_p and C_v are molar specific heats, then molar constant R is to be used in the equation i.e., above relation would be written as

$$C_p - C_v = \frac{R}{J}$$

5.5. Ratio of two specific heats.—The ratio of the two principal specific heats of a gas is a very important constant in thermodynamics and is denoted by γ (gamma). It is also known as adiabatic index.

$$\therefore \gamma = \frac{C_p}{C_v}$$

Since C_p is always greater than C_v therefore the value of γ is always greater than unity i.e., $\gamma > 1$

$$\text{Now } C_p = C_v + \frac{R}{J}$$

where R is gas constant in work units.

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{C_v + \frac{R}{J}}{C_v}$$

$$\text{or } \gamma = 1 + \frac{R}{JC_v}$$

$$\gamma - 1 = \frac{R}{JC_v}$$

$$\text{Hence } C_v = \frac{R}{J(\gamma - 1)} = \frac{AR}{(\gamma - 1)}$$

where $A = \frac{1}{J} = 0.24 \text{ cal/Joule}$

$$\text{Also } C_p = \gamma C_v$$

$$\therefore C_p = \frac{\gamma AR}{(\gamma - 1)}$$

If C_p and C_v represent the molar specific heats of a gas then the equations become

$$C_v = \frac{R}{J(\gamma - 1)} = \frac{AR}{(\gamma - 1)}$$

$$\text{and } C_p = \frac{\gamma R}{J(\gamma - 1)} = \frac{\gamma AR}{(\gamma - 1)}$$

5.6. Change in Internal Energy of a gas. When m gm. of a gas are heated from $t_1^\circ\text{C}$ ($T_1^\circ\text{K}$) to $t_2^\circ\text{C}$ ($T_2^\circ\text{K}$) the increase in its internal energy dE is given by

$$dE = mC_v(T_2 - T_1)$$

$$\text{But } C_v = \frac{AR}{\gamma - 1}$$

$$\therefore dE = \frac{mAR(T_2 - T_1)}{\gamma - 1} \quad \dots(i)$$

$$\text{Also } P_1V_1 = mRT_1$$

$$\text{and } P_2V_2 = mRT_2$$

$$\therefore P_2V_2 - P_1V_1 = mR(T_2 - T_1)$$

$$\text{or } mR(T_2 - T_1) = P_2V_2 - P_1V_1$$

Hence putting this value in equation (i), we have

$$\begin{aligned} dE &= \frac{A (P_2 V_2 - P_1 V_1)}{\gamma - 1} \text{ in heat units} \\ &= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} \text{ in work units} \end{aligned}$$

If gm.-mole of a gas is considered, then the equation (i) becomes

$$dE = \frac{MRA (T_2 - T_1)}{\gamma - 1} = \frac{RA (T_2 - T_1)}{\gamma - 1}$$

$$\therefore R = MR$$

If R is in heat units then,

$$dE = \frac{R(T_2 - T_1)}{\gamma - 1}$$

Example 1. Calculate the specific heat at constant volume for air, given that specific heat at constant pressure = 0.23. Density of air at 27°C and standard atmospheric pressure = 1.18 gms/litre and $J = 4.2$ joules/cal. Given that $g = 981 \text{ cm/sec.}^2$ and density of mercury is 13.6 gms/c.c. (P. U.)

Mass of 1 litre of air = 1.18 gms.

Pressure of air $P = 76 \text{ cms. of Hg.}$

$$= 76 \times 13.6 \times 981 \text{ dynes/sq. cm.}$$

$$= 1.013 \times 10^6 \text{ dynes/sq.cm.}$$

Temperature of air $T' = 273 + 27 = 300^\circ K.$

Now $PV = mRT$

$$\text{or } P = \frac{m}{V} RT = \rho RT'$$

$$\text{or } R = \frac{P}{\rho T'}$$

where ρ = density of air = mass per unit volume in gms. per c.c.

$$= \frac{1.18}{1000} \text{ gm/c.c.}$$

Substituting the values we have

$$R = \frac{1.013 \times 10^6}{\frac{1.18}{1000} \times 300}$$

or

$$\frac{R}{J} = \frac{1.013 \times 10^6}{\frac{1.18}{1000} \times 300} \times \frac{1}{4.2 \times 10^7} = 0.06821$$

$$\text{But } c_p - c_v = \frac{R}{J}$$

$$\begin{aligned}\text{or } c_v &= \text{specific heat per gm. at constant volume} = c_p - \frac{R}{J} \\ &= 0.23 - 0.06821 \\ &= 0.1618\end{aligned}$$

Example 2. The specific heat of Argon at constant pressure is 0.127 and the ratio of its specific heats is 1.667. Calculate the mechanical equivalent of heat. One litre of argon at 0°C and 76 cm, pressure weighs 1.786 gm. Given that $g=981 \text{ cm./sec}^2$ and density of mercury = 13.6 gms/c.c. (A.M.I.E.)

According to general gas equation

$$PV = mRT$$

$$\text{or } P = \frac{m}{V} RT = \rho RT$$

$$\therefore R = \frac{P}{\rho T} \quad \dots(i)$$

given that at N.T.P.

$$P = 76 \times 13.6 \times 981 \text{ dynes/sq. cm.}$$

$$= 1.013 \times 10^6 \text{ dynes/cm}^2$$

$$T = 273^\circ K$$

$$\rho = \frac{m}{V} = \frac{1.786}{1000} = 1.786 \times 10^{-3} \text{ gm/cm}^3$$

Substituting the values in relation (i), we have

$$R = \frac{1.013 \times 10^6}{1.786 \times 10^{-3} \times 273} = 2.08 \times 10^6 \text{ ergs/gm/}^\circ K.$$

$$\text{Given } c_p = 0.127 \text{ and } \frac{c_p}{c_v} = 1.667$$

$$\text{or } c_v = \frac{0.127}{1.667} = 0.077.$$

$$\text{Now } c_p - c_v = \frac{R}{J}$$

$$\begin{aligned}\text{or } J &= \frac{R}{c_p - c_v} = \frac{2.08 \times 10^6}{0.127 - 0.077} \\ &= 4.16 \times 10^7 \text{ ergs/cal.} \\ &= 4.16 \text{ joules/cal.}\end{aligned}$$

Example 3. If one litre of Hydrogen weighs 3.09 gm, at N.T.P. and if its specific heat at constant pressure is 3.409, find the ratio of c_p and c_v . $J = 4.18 \text{ joules/cal.}$

$$\text{Now } PV = mRT$$

$$\text{or } P = \frac{mRT}{V} = \rho RT$$

$$\text{or } R = \frac{P}{\rho T}$$

At N.T.P.

Pressure $P = 1.013 \times 10^6$ dynes/cm²

and temp. $T = 273^\circ K$.

$$\rho = \frac{0.09}{1000}$$

$$\therefore R = \frac{1.013 \times 10^6}{\frac{0.09}{1000} \times 273} = 4.12 \text{ joules/gm/}^\circ K$$

$$\text{Now } c_p - c_v = \frac{R}{J}$$

$$\begin{aligned} \text{or } c_v &= c_p - \frac{R}{J} = 3.409 - \frac{4.12}{4.18} = 3.409 - 0.9856 \\ &= 2.4234 \end{aligned}$$

$$\therefore \gamma = \frac{c_p}{c_v} = \frac{3.409}{2.4234} = 1.41$$

Example 4. Calculate the specific heat at constant volume for hydrogen, given that its specific heat at constant pressure is 6.85 cal/gm molecule. Density of hydrogen at N.T.P. is 0.0899 gm/litre and $J = 4.19$ joules/cal.

The gram molecular specific heat of hydrogen at constant pressure $C_p = 6.85$ cal/gm mol.

Density of hydrogen at N.T.P. = 0.0899 gm/litre.

The molecular weight of H_2 is 2.

\therefore Volume occupied by one gm. molecule of gas at N.T.P.

$$V = \frac{1000}{0.0899} \times 2 = 22430 \text{ c.c.}$$

Pressure at N.T.P. = $76 \times 13.9 \times 981$ dynes/cm² = 1.031×10^6 dynes/cm²

Temperature at N.T.P. = $0^\circ C = 273^\circ K$.

Applying the equation

$$\begin{aligned} R &= \frac{PV}{T} = \frac{1.031 \times 10^6}{273} \times \frac{1000 \times 2}{0.0899} \\ &= 8.318 \text{ joules/gm. mol/}^\circ K. \end{aligned}$$

Specific heat at constant volume $C_v = C_p - \frac{R}{J}$

$$= 6.85 - \frac{8.318}{4.2}$$

$$= 6.865 - 1.985$$

$$= 4.865 \text{ cal/gms mol.}$$

Example 5. Calculate the difference in two specific heats of one gm. of Helium. Molecular weight of Helium = 4.

Mol. wt. of Helium = 4

one gm. mol. of every gas at N. T. P. occupies 22.4 litres
= 22400 c. c.

Hence volume of 4 gms of Helium at N. T. P. = 22400 c. c.

∴ Volume of 1 gm of Helium at N.T.P. = $\frac{22400}{4} = 5600$ c.c.

Pressure $P = 76$ cms of Hg.

Temperature $T = 0^\circ\text{C} = 273^\circ\text{K}$.

Hence $R = \frac{PV}{T} = \frac{76 \times 13.6 \times 981}{273} \times 5600 = 2.078$ joules/gm/ 1°K

Also $J = 4.2$ joules/cal.

But $c_p - c_v = \frac{R}{J} = \frac{2.078}{4.2} = 0.5$ approx.

5.7. Joly's differential Steam Calorimeter for the determination of specific heat at constant volume. This apparatus was devised by Prof. Joly for measuring the specific heat of a gas at constant volume. This method depends upon the principle that heat lost by hot substance is equal to the heat absorbed by cold substance. In this method steam is passed to raise the temperature of the enclosed gas at constant volume. As steam loses heat, it condenses. The heat lost by steam while condensing is equal to the amount of heat gained by the gas,

The apparatus consists of a double walled metal enclosure M known as steam chamber. It is placed below a sensitive balance B . Two exactly identical hollow copper spheres h_1 and h_2 of about 6.7 cm in dia. and capable of withstanding a pressure of about 35–40 atmospheres are freely suspended from either arm of the balance, by fine wires of platinum pp . Each sphere is provided with a small tray t at the bottom known as "catch water" to hold the condensed steam and is provided with a "shelter" S above it so that steam condensed on the ceiling of the chamber may not fall on the sphere or catch water. The holes H . H . through which wires pp carrying spheres enter the steam chamber are made narrow so that any steam escaping through them may not disturb the weighing and are lined with plaster of Paris for preventing the formation of water drops at the holes so that these do not cause an error in weighing. The formation of water drops due to the condensation of steam on the suspension wires, in the holes, is further prevented by placing small heating coils c . c . around the suspension wires as shown in Fig. 5.2. These coils are heated by passing an electric current and thus prevent the condensation of steam.

Both the spheres are thoroughly cleaned from inside and evacuated. They are then counterpoised on the balance. Now one of the spheres say h_1 , is exhausted and the sphere h_2 is filled with the gas under test at a high pressure. It is again counterpoised against, the

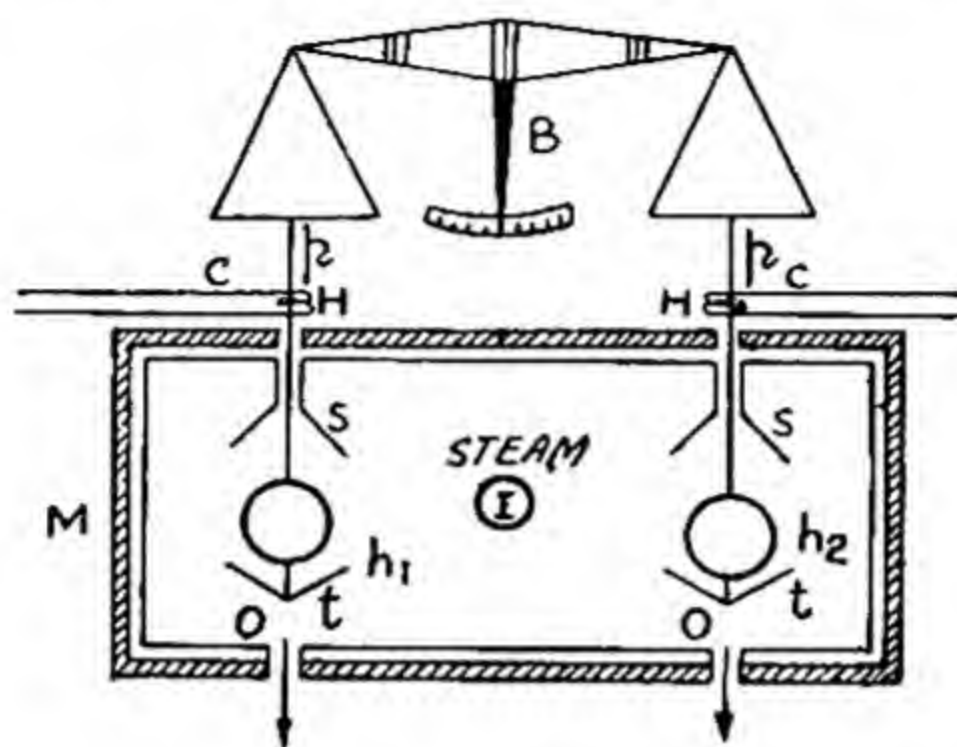


Fig. 5.2.

empty sphere and thus the mass of the gas in h_2 is found out. Let it be m gms. The initial temperature t_1 of the steam chamber is determined by a sensitive thermometer. Now dry steam is admitted into the steam chamber through the inlet hole I at the back and leaves at the bottom at $O.O$. The steam starts condensing on both the spheres until they come to the temperature of the steam. More of steam condenses on the sphere h_2 than on the sphere h_1 because in the case of h_2 it has to heat the gas also. When steady condition is reached and no further condensation of steam occurs, additional weights are added in the pan attached to sphere h_1 until the two spheres are again counterpoised.

These weights give the weight w of the extra steam condensed on the gas filled sphere h_2 to heat the contained gas to the temperature of steam. The temperature of steam t_2 is also noted. Both the spheres are exactly similar and so they have same thermal capacities.

Let C_v be the specific heat of the gas at constant volume and L the latent heat of steam, then

$$\text{Heat gained by the gas} = m C_p (t_2 - t_1) \text{ cal}$$

$$\text{Heat lost by steam} = wL$$

$$\text{But Heat gained} = \text{Heat lost}$$

$$\therefore m C_v (t_2 - t_1) = wL$$

$$\text{or } C_v = \frac{wL}{m(t_2 - t_1)}$$

For getting accurate result the following corrections have to be applied.

1. The first weighing is taken in air at atmospheric pressure at $t_1^\circ\text{C}$ whereas the second weighing is made in steam at $t_2^\circ\text{C}$. Hence it is necessary to reduce both the weighings to vacuum to avoid error due to buoyancy.

2. It is impossible to get two spheres of exactly same size and thermal capacity. To avoid the error due to this factor, repeat the experiment by evacuating h_2 and filling h_1 with same gas at same pressure and temperature. Calculate C_v in this case. The mean value of both the specific heats will give correct value.

3. The sphere containing the gas expands, both due to the rise in its temperature and also due to increased pressure of the enclosed gas. Some work is thus done against external pressure so that the calculated value of C_v is rather too high. Correction has to be applied for it.

4. Correction for the change in buoyancy arising from the increased volume of the sphere must also be applied.

Example 6. In Joly's steam calorimeter the difference in weights of the steam condensed when the copper sphere is filled with the gas at 15 atmospheres pressure and when exhausted is 0.38 gm. If the volume of the gas contained in the sphere is 1000 c.c. and its density is 0.008 gm./c.c., calculate the specific heat at constant volume. The initial temperature of the gas is 15°C and the temp. of the steam equal to 100°C . Latent of steam is 540 cal./gm.

Volume of the gas $= 1000 \text{ c.c.}$

Density of the gas $= 0.008 \text{ gm./c.c.}$

\therefore mass of the gas $= \text{volume} \times \text{density}$ $M = 1000 \times 0.008$
 $= 8 \text{ gm.}$

Initial temperature $t_1 = 15^\circ\text{C}$

Temperature of the steam $t_2 = 100^\circ\text{C}$

Latent heat of steam $L = 540 \text{ cal./gm.}$

mass of steam condensed $m = 0.38 \text{ gm.}$

Let C_v be the specific heat of the gas at constant volume.

Hence applying the formula we have

$$C_v = \frac{mL}{M(t_2 - t_1)} = \frac{0.38 \times 540}{8(100 - 15)} = 0.3$$

5.8. Determination of Specific heat at constant pressure. Regnault's experiment. An accurate method of measuring specific heat at constant pressure was devised by **Regnault**. It depends upon the principle that

heat lost by hot substance is equal to heat gained by cold substance when the two substances having no chemical interaction are mixed together.

The apparatus consists of a reservoir R containing pure and dry gas compressed in it. The temperature of the reservoir is kept constant by surrounding it by a large water tank as shown in Fig. 5.3. A thermometer T_1 measures the temperature of water in the tank. The pressure of the gas in the reservoir can be measured with a manometer M_p .

The gas is allowed to flow continuously at constant pressure by opening the tap and regulating the valve RV .

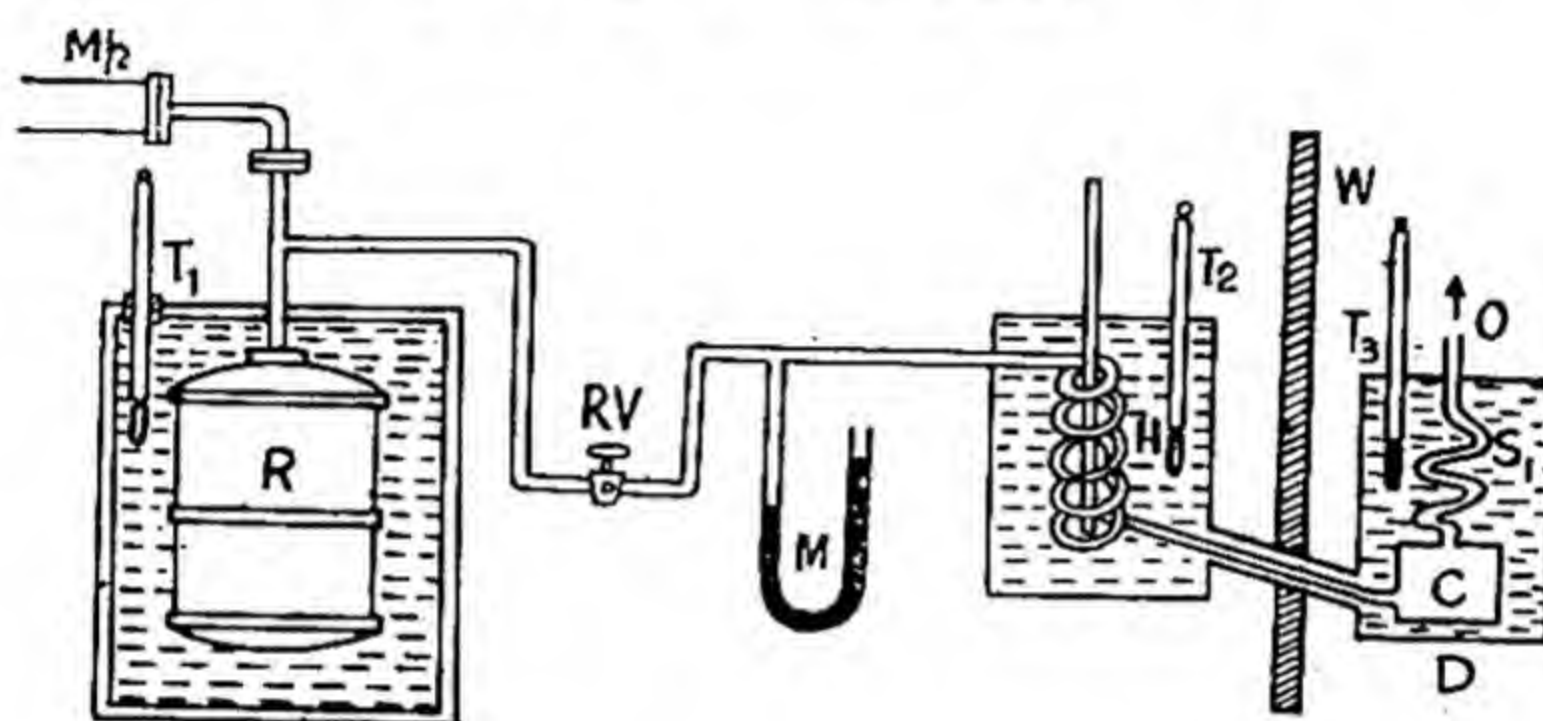


Fig. 5.3

This is achieved by opening the valve more and more as the pressure of the gas in the reservoir goes down, so that the manometer M records a small but constant difference of pressure.

The gas then flows through the heating spiral H immersed in hot oil bath kept at constant temperature. A thermometer T_2 is suspended in oil bath to find its temperature. The spiral is sufficiently long so that the gas while passing through the spiral attains the temperature of the oil bath. After passing through the spirals, the gas is made to pass through the tube C into a copper spiral S_1 placed in a calorimeter D containing water and thermometer T_3 . The gas finally escapes into air through an outlet O . In this process the gas gives its heat to water and is itself cooled to the temperature of water. It is very essential that the gas should flow through the heating spiral H and through the copper spiral S_1 uniformly under constant pressure. As the gas escapes, the pressure of the gas in the reservoir goes down and thus it does not flow under constant pressure. This is avoided by continuously adjusting the regulating valve RV . As the gas escapes through the outlet O , the valve is gradually opened more and more so as to have a wider passage, thus making the gas flow under constant pressure. This is ensured by the manometer M which always gives the same difference in the levels of the mercury in the two limbs.

In order to avoid the loss of heat by the gas in passing from the bath to the calorimeter, the calorimeter is placed inside a double walled vessel filled with water to minimise the loss of heat due to radiation etc. In order that the gas may enter the calorimeter at the temperature of the oil bath, it is placed as near the bath as possible. A wooden screen W is interposed between oil bath and calorimeter so as to minimise error due to gain of heat by radiation from oil bath.

Let t_1 = the temperature of the hot bath

t_2 and t_3 = the initial and final temperatures of the water in the calorimeter

w = water equivalent of the calorimeter and its contents

M = mass of the water in the calorimeter

Heat gained by the calorimeter and its contents

$$= (w + M)(t_3 - t_2) \text{ cal.}$$

The temperature of the hot gas falls through $(t_1 - t_2)$ in the beginning and through $(t_1 - t_3)$ at the end as the temperature of the calorimeter and its contents goes on slowly rising from t_2 to t_3 due to the passage of the hot gas, the average fall of temperature of the gas during the experiment

$$= \frac{(t_1 - t_2) + (t_1 - t_3)}{2} = \left(t_1 - \frac{t_2 + t_3}{2} \right)$$

If

m = mass of the gas escaped

and

C_p = specific heat of gas at constant pressure,

then

$$\text{Heat lost by the escaped gas} = m C_p \left(t_1 - \frac{t_2 + t_3}{2} \right)$$

$$\therefore \text{Heat gained} = \text{Heat lost}$$

$$\therefore (M + w)(t_3 - t_2) = m C_p \left(t_1 - \frac{t_2 + t_3}{2} \right)$$

or

$$C_p = \frac{(w + M)(t_3 - t_2)}{m \left(t_1 - \frac{t_2 + t_3}{2} \right)}$$

The mass of the gas that escapes from the reservoir is found by noting the pressure of the gas in the beginning and at the end of the experiment when the gas is maintained at the constant temperature $T^\circ K$.

Let initial pressure of the gas in the reservoir = P_1

Final pressure of the gas in the reservoir = P_2

Temperature of the gas $= T^{\circ}K$

Density of the gas at N.T.P. $= \rho_0$

Volume of the reservoir $= V$

Now the density of a gas is directly proportional to the pressure and inversely proportional to the absolute temperature.

\therefore Density of the gas at pressure P_1 and temperature T

$$\rho_1 = \rho_0 \frac{P_1}{P_0} \times \frac{T_0}{T}$$

where P_0 and T_0 are normal pressure and temperature on the absolute scale of temperature.

$$\therefore \rho_1 = \rho_0 \frac{P_1}{76} \times \frac{273}{T} \quad \dots(i)$$

Similarly the density ρ_2 at the pressure P_2 is given by

$$\rho_2 = \rho_0 \frac{P_2}{76} \times \frac{273}{T} \quad \dots(ii)$$

From (i) and (ii), we have

$$\rho_1 - \rho_2 = \frac{\rho_0 (P_1 - P_2) 273}{76 \times T}$$

\therefore the mass of the gas

$$\begin{aligned} m &= (\rho_1 - \rho_2) V \\ &= \frac{P_0 (P_1 - P_2) 273}{76 \times T} \times V \end{aligned}$$

Knowing every quantity on the right hand side, m can be calculated.

Example 7. In an experiment for the determination of the specific heat at constant pressure by Regnault's method.

Temperature of the oil bath $t_1 = 250^{\circ}C$

Initial temperature of water in the calorimeter $t_2 = 27^{\circ}C$

Final temperature of water after passing hot air in the calorimeter $t_3 = 37^{\circ}C$

Water equivalent of calorimeter and its contents $w = 10.52$ gms

Mass of water taken in the calorimeter $M = 50.43$ gms

Constant temperature of the bath containing the gas holder $t = 27^{\circ}C$

Density at N.T.P. $\rho = 0.001293$ gm/c.c.

Capacity of the gas holder $V = 50$ litres.

Decrease of pressure of air after the experiment $P_1 - P_2 = 15.2$ cm. of H_g

Calculate the mass of air passing through the calorimeter and also its specific heat at constant volume.

The mass of air passing through the calorimeter

$$m = \frac{\rho_o(P_1 - P_2)273}{76 \times T} \times V$$

$$= \frac{0.001293 \times 15.2 \times 273}{76 \times (273 + 27)} \times 50000 = 11.77 \text{ gms.}$$

Specific heat of air at constant pressure.

$$C_p = \frac{(w + M)(t_3 - t_2)}{m \left(t_1 - \frac{t_2 + t_3}{2} \right)}$$

$$= \frac{(10.52 + 50.43)(37 - 27)}{11.77 \left[250 - \frac{37 + 27}{2} \right]} = \frac{60.95 \times 10}{11.77 \times 218}$$

$$= 0.237$$

5.9. Scheel and Huese continuous flow method for the determination of C_p . Regnault determined the specific heat of a gas at a constant pressure by allowing it to flow into a vessel where it was heated to high temperature, and then passing it at constant pressure into another vessel inside a calorimeter and water, which rose in temperature. A much more accurate method of determination of C_p , however consists in using the same technique with a gas as was used in determining the specific heat of a liquid by Callender and Barne's continuous flow (electric) method. This method has been designed by **Scheel and Huese** for finding the C_p of a gas.

The apparatus consists of a glass tube of special shape as shown in the Fig. 5.4.

In the innermost part of the tube there is a coil of platinum

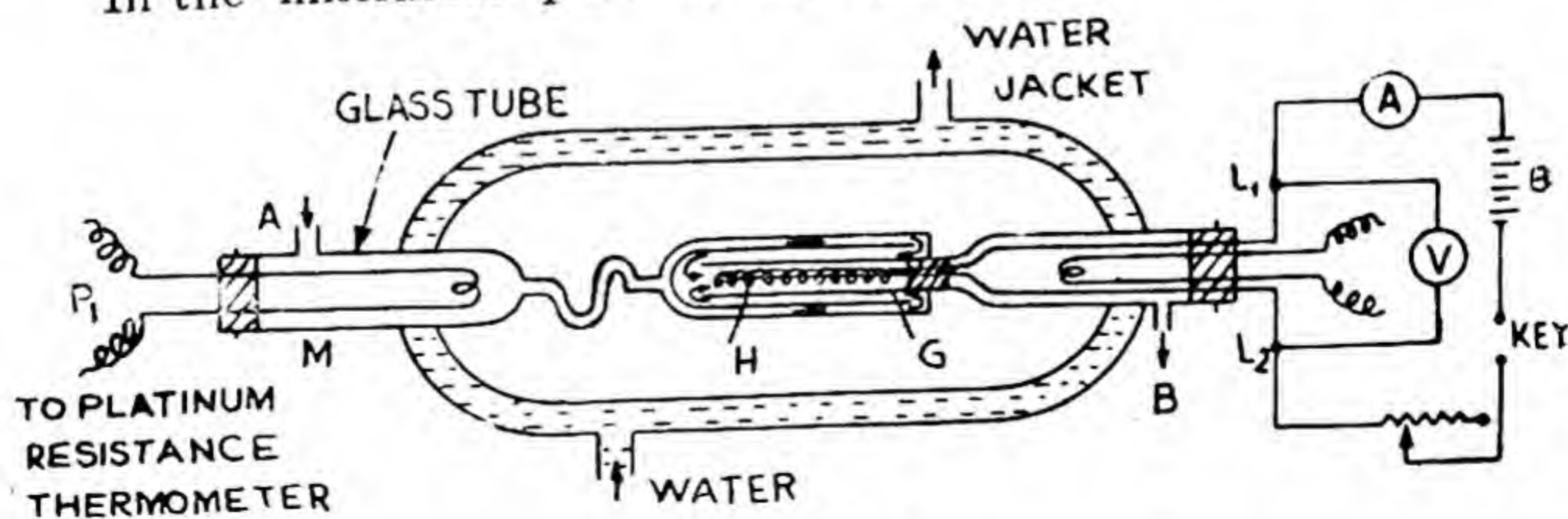


Fig. 5.4

wire H , which is sealed into the glass and is heated by connecting the

leads L_1 and L_2 to a battery B through a rheostat a key and an ammeter A . The potential difference is measured by connecting the voltmeter V across the leads L_1 and L_2 .

The glass tube is sealed into an outer vacuum jacket to reduce the loss of heat due to radiation. The gas enters the glass tube through a long metal tube M in which is sealed a platinum resistance thermometer P_1 which measures its initial temperature. A similar platinum resistance thermometer is fitted on the other side to measure the temperature of the out going gas.

To begin the experiment, the apparatus is placed in a constant temperature bath. A steady flow of gas at constant pressure is introduced into the metal tube at A and its temperature is measured by thermometer P_1 . The gas then flows through spiral tube and then travels in the direction of the arrows through the zig-zag path and finally comes in contact with the heating element. The purpose of providing the zig-zag path is that any heat lost by the heated gas is brought back into it by the incoming stream of the gas and there is no wastage.

The gas then passes through copper gauze G , the function of which is to mix the gas thoroughly so that it attains a uniform temperature. The gas finally flows over a second thermometer and it issues out at B .

When the steady state is reached the constant rise in temperature of the gas is found by taking the readings of the two platinum resistance thermometers at the entrance and exit respectively. Let temperatures recorded by these thermometers be t_1 and $t_2^\circ\text{C}$. respectively. The mass of the gas passing through the calorimeter per second m , is measured by noting the initial and the final pressures of the gas in the reservoir. If V be the reading of the voltmeter, I that of the ammeter, then heat produced electrically by the

wire $H = \frac{VIt}{4.2}$ calories

When the current flows for t seconds

Heat taken up by the gas $= mC_p (t_2 - t_1)$

Neglecting losses we have

$$mC_p (t_2 - t_1) = \frac{VIt}{4.2}$$

$$\text{or } C_p = \frac{VIt}{4.2m (t_2 - t_1)}$$

Advantages. (i) The loss of heat due to radiation is very small and hence can be neglected for all practical purposes.

(ii) The amount of heat generated can be measured accurately as it is produced electrically.

(iii) Since the temperatures are constant the thermal capacity of the apparatus can be neglected. Moreover, steady temperatures can be read with greater accuracy than the varying temperatures.

(iv) The method can be used to study the variations of specific heat with temperature. To find the specific heat at very low temperatures, the gas is initially passed through a low temperature bath in which the whole apparatus is also immersed. In case of helium and other rare gases, Scheel and Huese further modified the apparatus so as to have a closed circuit.

Expected Questions.

1. (a) How would you account for the two specific heats of a gas? (A.M.I.E.)
(b) Explain why the specific heat of a gas at constant pressure is greater than at constant volume, obtain an expression for the difference between the values for a perfect gas. (A.M.I.E.)
2. Describe an accurate method of measuring the specific heat of a gas at constant pressure.
3. Describe Joly's steam calorimeter and explain how it may be used for determining the specific heat of a gas at constant volume.
4. Give an account of the continuous flow method of measuring the specific heat of a gas at constant pressure and point out its advantages.
5. What is meant by specific heat? How does the change of the temperature scale effect the numerical values.

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CHAPTER VI

THE MECHANICAL EQUIVALENT OF HEAT

6.1. Thermodynamics. *It is the science that discusses the relation of heat to mechanical work. It establishes the equivalence between work done and the heat produced.*

6.2. First law of Thermodynamics. According to this law, when a given amount of work is done, an equivalent amount of heat is produced. When a certain quantity of heat disappears, an equivalent amount of work is always obtained. Thus we are perfectly justified in saying that besides kinetic and potential energies of matter there is another form of energy called **heat energy**. The relation between work done and heat produced is expressed in the First law of thermodynamics which is stated after Maxwell as follows.

“When mechanical work is completely converted into heat or heat is completely converted into mechanical work, then for each unit of work which is converted into heat, a definite quantity of heat is produced and for each unit of heat converted into work a definite quantity of work is furnished.”

Or

“Whenever work is transformed into heat or heat into work, the quantity of work is mechanically equivalent to the quantity of heat.”

If W is the amount of mechanical work which when completely converted into heat produces H units of heat, then it is found that

$$W \propto H$$

or

$$\frac{W}{H} = \text{constant}$$

The constant is known as Joule's mechanical equivalent of heat and is denoted by J .

∴

$$\frac{W}{H} = J$$

If H = unit quantity of heat then $J = W$. Thus Joule's mechanical equivalent of heat may be defined as the amount of work which must be done to produce a unit quantity of heat.

Units of J.

On C.G.S. system of units the work W is measured in ergs and heat H in calories. The value of J on this system is 4.2×10^7 ergs per calorie.

or $J = 4.2 \times 10^7$ ergs per cal.

On M.K.S. system of units the work W is measured in Joule's and heat H in calories or kilo-calories.

The value of $J = 4.2$ Joules/calorie
 $= 4200$ Joules/kilo-calorie

Also if W is measured in Kg.-metre and H is in Kilo.cal. then the value of J is $\frac{4200}{9.81}$ kg. metre/kilo-cal. or **426.8 kg. metre/kilo-cal.**

Note. 1 Kilo cal. = 426.7 kg.-metre and 1 kg. meter = 9.81 joules.

Example 1. A water fall is 420 m. high. Assuming that no energy is lost by water, find how much hotter the water at the bottom is than that at the top $J = 4.2$ Joules/cal. and $g = 9.81$ m/sec².

Let m kg. of water fall through a height h and the temperature rises through $t^\circ\text{C}$

Work done when m kg. fall through a height h

$$W = mgh \text{ Joules.}$$

$$= m \times 9.81 \times 420 \text{ Joules.}$$

Specific heat of water $S = 1$

If H is the heat generated, then

$$H = mSt = mt \text{ Kilo-cal.}$$

But $W = JH$.

where $J = 4.2$ Joules/cal.
 $= 4200$ Joules/Kilo-cal.

$$\therefore m \times 9.81 \times 420 = 4200 \times m \times t.$$

$$\text{or } t = \frac{9.81 \times 420}{4200} = 0.981^\circ\text{C}$$

Example 2. A lead bullet at a temperature of 47°C strikes against an unyielding target. If the heat produced by sudden stoppage is just sufficient to melt the bullet, with what velocity does the bullet strike the target. It is assumed that all the heat is produced within the bullet.

Melting point of lead = 327°C , specific heat of lead = 0.03 cal/gm/ $^\circ\text{C}$

Latent heat of fusion of lead = 6 cal/gm. $J = 4.2$ Joules/cal.

Let m kg. be the mass of the bullet.

Heat required to raise the temperature of the bullet from 74°C to $327^{\circ}\text{C} = m \times 0.03 \times (327 - 47) = 8.4 m$ kilo-cals. $= 8400m$ cals.

Heat required for melting $= m \times 6 = 6m$ kilo-cal. $= 6000 m$ cals.

Total heat required for melting $H = (8.4m + 6m)$
 $= 14.4m$ kilo-cals. $= 14400 m$ cals.

Kinetic energy of the bullet $W = \frac{1}{2}mv^2$ joules.

where v is the velocity in metres/sec.

But $W = JH.$

$$\therefore \frac{1}{2}mv^2 = 4.2 \times 14400m$$

$$\text{or } v^2 = 4.2 \times 2 \times 14400$$

$$\therefore v = \sqrt{28800 \times 4.2} = 348 \text{ m/sec.}$$

Example 3. From what height must a block of ice drop in order that it may be melted completely. It is assumed that 50% of the energy of fall is retained by the ice.

Let m be the mass of ice and h the height from which it is dropped, then

$$\begin{aligned} \text{Amount of work done } W &= mgh = m \times 980 \times h \text{ ergs.} \\ &= m \times 980 \times h \times 10^{-7} \text{ joules.} \end{aligned}$$

$$\text{Energy utilized to produce heat} = \frac{50}{100} \times m \times h \times 980 \times 10^{-7} \text{ joules.}$$

Heat required to melt m gms of ice $H = m \times 80$ cals.

$$\therefore H = \frac{W}{J}$$

$$m \times 80 = \frac{\frac{1}{2} \times m \times h \times 980 \times 10^{-7}}{4.2}$$

$$\text{or } h = \frac{80 \times 4.2 \times 10 \times 2}{980} = 6860000 \text{ cms.}$$

$$= 68.6 \text{ K. metres}$$

Example 4. A closed card board tube one metre long contains some lead shots at one end. The tube is quickly inverted so that shots fall through the whole length of the tube. The operation is repeated 100 times. Find the rise in temperature if the specific heat of lead is 0.03; take $g = 9.81 \text{ m./sec}^2$. (P.U.)

Let the mass of lead shots $= m$ kgm.

Work done when the shots fall 100 times in the card board tube through a height of 1 metre

$$\begin{aligned} W &= n mgh \text{ joules} \\ &= 100 \times m \times 9.81 \times 1 \text{ joules.} \\ &= 981 m \text{ joules} \end{aligned}$$

Let t be the rise in temperature of lead shots of specific heat 0.03, then

$$\begin{aligned} \text{Heat produced} &= mSt \\ &= m \times 0.03 \times t \text{ kilo-cals.} \end{aligned}$$

The card-board is a bad conductor and does not take up any heat.

$$\begin{aligned} \text{Now} \quad W &= JH \\ \text{where} \quad J &= 4200 \text{ Joules/kil-cal.} \\ \therefore 981 m &= 4200 \times m \times 0.03 \times t \\ \text{or} \quad t &= \frac{981}{4200 \times 0.03} \\ &= 7.78^\circ\text{C} \end{aligned}$$

Example 5. A feed pump delivers 1200 litres of water per hour against a constant head of 100 metres. What is the work done per hour in heat units.

\therefore Quantity of water raised per hour = 1200 litres = 1200 kg.

$$\begin{aligned} \text{Work done by pump per hour} &= Mgh \\ &= 1200 \times 100 \text{ kg. metre} \end{aligned}$$

Now 1 Kilo-cal. = 426.7 kg. metre

$$\begin{aligned} \therefore \text{Work done per hour in heat units} &= \frac{\text{Work done in kg. metre}}{426.7} \text{ Kilo-cals.} \\ &= \frac{1200 \times 100}{426.7} = 281.3 \text{ kilo-cals.} \end{aligned}$$

6.3. Determination of Mechanical equivalent of Heat. The following methods are commonly used for determining the value of J .

1. Joule's Experiment.
2. Rowland's Experiment.
3. Calender and Barne's continuous flow method.
4. Callender's Brake Band Method.
5. Electrical method and
6. Searle's Friction Cone method.

(1) **Joule's experiment for finding J.** The apparatus used by **Joule** is shown in Fig. 6.1. It consists of a large calorimeter C to the sides of which are soldered vanes VV . The calorimeter is provided with a water-tight lid having a hole in its centre through

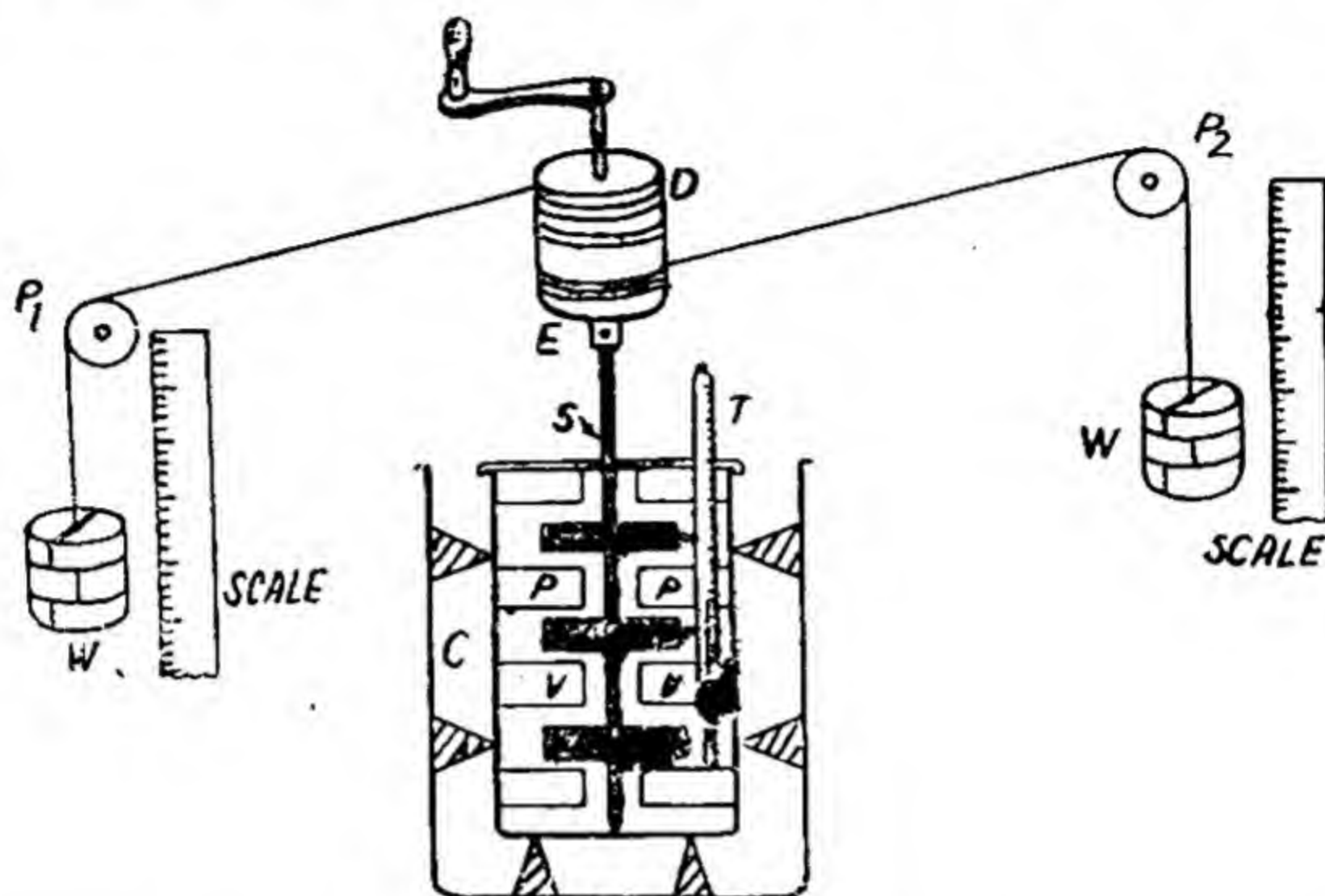


Fig. 6.1.

which passes the spindle S . The spindle carries paddles PP which can rotate in between the corresponding openings in the fixed vanes. The vanes prevent the rotation of water along with the revolving paddles. The spindle S is connected with a removable pin E to a drum D and can be connected or disconnected from the drum by fixing or removing the pin when desired. Two cords are wound round the drum in such a way that their free ends leave it in the opposite directions but rotate the drum in the same direction. These cords pass over friction less pulleys P_1 and P_2 and to their free ends are attached two equal weights W, W . A handle is connected at the top of the drum. The vertical distance through which the weights fall is measured with the help of scales placed on both sides of the apparatus. A known mass of water is put in the calorimeter and its temperature is recorded with a sensitive thermometer T placed in it.

When the weights are allowed to fall the spindle turns and the paddles produce a churning motion of the water inside the calorimeter. The potential energy of the weights is converted into the kinetic energy of water. The motion of water is prevented by vanes and thus the kinetic energy of water is converted into heat energy. As the weights reach the ground, the pin E is removed, the spindle is disconnected and the weights are brought back to their initial position by rotating the drum with the help of the handle. The pin E is once again fixed and the weights are allowed to fall as before. This process is repeated a number of times and the tempera-

ture of the calorimeter is once again recorded. The difference of the two readings give the rise in temperature of calorimeter and its contents.

Let m be the mass of water in gms., w the water equivalent of calorimeter, vanes, spindle and paddles and t be the rise in temperature.

Heat produced $H = (m + w) t$ calories

Let M gms. be the mass of each weight falling n times through a height h cms. during the experiment,

\therefore Work done $W = 2Mgh \times n$ ergs

Assuming that no heat is lost by radiation and other causes, the mechanical equivalent of heat,

$$J = \frac{W}{H} = \frac{2Mgh \times n}{(m + w) t}$$

As the work is measured in ergs and heat in calories, the value of J on the C.G.S. system expressed in ergs per calorie. If m and w are measured in kilo-gms, H will be in kilo-cals. If M is in kilo-gms, h in metres and g in metres per sec² then W is in joules. Hence the value of J in M.K.S. system is measured in joules per kilo-cal.

Sources of error. This method does not give accurate results due to following errors :—

- (i) Loss of heat by radiation.
- (ii) Loss of energy due to friction of pulleys.

(iii) *Kinetic energy of the falling weight.* The whole of the potential energy of the falling weights is not converted into work but a part of it is utilised in giving a kinetic energy to these weights themselves. If V be the velocity of each weight as it reaches the ground, the kinetic energy of each weight in one fall = $\frac{1}{2} MV^2$, the kinetic energy of both weights in one fall,

$$= \frac{1}{2} MV^2 \times 2 = MV^2$$

The kinetic energy of both weights in n falls

$$= nMV^2$$

\therefore Net work done $W = 2Mghn - nMV^2$

Hence

$$J = \frac{(2Mgh - MV^2)n}{(m + w)t}$$

Example 6. In Joule's experiment a mass of 1.45 k.gms. was allowed to fall through a height of 30 cms. The process was repeated 200 times and the rise of temperature observed was 2.0°C. If the thermal capacity of the calorimeter and its contents is 100, find the value of J .

Let M be the mass in gms. falling n times through a height h during the experiment.

$$M = 1.42 \text{ kgms.} = 1420 \text{ gms.}$$

$$\text{Height } h = 30 \text{ cms.}$$

$$\text{No. of falls } n = 200$$

Work done by the falling mass,

$$\begin{aligned} W &= Mgh \times n \text{ ergs} \\ &= 1420 \times 980 \times 30 \times 200 \text{ ergs} \\ &= 1420 \times 980 \times 30 \times 200 \times 10^{-7} \text{ joules} \end{aligned}$$

Thermal capacity of the calorimeter and its contents
 $= 100$

Rise in temperature $t = 2^\circ\text{C}$

\therefore Heat produced $H = 100 \times 2 = 200 \text{ cal.}$

$$\begin{aligned} \text{Hence } J &= \frac{W}{H} = \frac{1420 \times 980 \times 30 \times 200 \times 10^{-7}}{200} \\ &= 4.18 \text{ joules/calorie.} \end{aligned}$$

(2) **Rowland's Experiment.** It is an improvement of Joule's method. Rowland tried to remove the following weak points in Joule's determination of mechanical equivalent of heat.

(i) The rise of temperature was small.

(ii) The mercury thermometer was not compared with a standard thermometer.

(iii) It was assumed that the specific heat of water between $0-100^\circ\text{C}$ was constant.

Description. The apparatus consists of a calorimeter C fitted with a set of vanes VV . A vertical shaft AB is suspended by a torsion wire T from a torsion head H . A set of paddles P, P attached to the shaft is made to rotate inside the calorimeter by means of an axle passing from below and connected to a steam engine. The number of rotations made by the axle is recorded by a revolution counter. The friction of water tends to make the calorimeter rotate along with the paddles and thus exerts a couple on the shaft AB . The paddles and the vanes have a very large number of holes drilled in them in order to make their churning action more thorough. The calorimeter contains a known mass of water and its temperature is measured by a sensitive thermometer T placed inside the perforated axle carrying the paddles. The calorimeter C is surrounded by a water jacket to measure the loss of heat due to radiation.

The shaft AB passes through the centre of a circular disc D to which it is firmly attached. Two silk cords are wound round the disc.

$$W = [\text{Moment of the couple}] \times [\text{angle turned in radians/sec.}]$$

$$= Mgd \times 2\pi n$$

If m is the mass of the water and w the water equivalent of the calorimeter, paddles and vanes etc. and $(t_2 - t_1)$ the rise of temperature then the heat absorbed.

$$H = (m + w)(t_2 - t_1)$$

$$\therefore J = \frac{W}{H} = \frac{Mgd \times 2\pi n}{(m + w)(t_2 - t_1)}$$

If M is in gms, d in cms. and g in cms. per sec², then W is in ergs. If m and w are in gms, then H is in calories. Therefore on the C.G.S. system J is measured in ergs per calorie.

If M is in K.gms, d in metres and g in metres per sec², then W is in Joules. If m and w are in K-gms, then H is in kilo-cals. Therefore on the M.K.S. system J is measured in Joules per kilo-cal.

(3) **Callender and Barne's Continuous flow Method.** The method has already been fully explained in the **Chapter on Specific Heat**. The only difference lies in the fact that instead of finding the specific heat, the value of J is found and from the two equations given in **Art. 4.9**, we have

$$mS(t_2 - t_1) + h = \frac{VIt}{J} \quad (i)$$

$$\text{and } m'S(t_2 - t_1) + h = \frac{V'I't}{J} \quad (ii)$$

Subtracting (i) from (ii), we have.

$$S(m - m')(t_2 - t_1) = \frac{1}{J}(VI - V'I')t$$

$$\text{or } J = \frac{(VI - V'I')t}{S(m - m')(t_2 - t_1)}$$

If V and I are measured in volts and amperes respectively then J is in Joules/cal.

Example 7. In an experiment by continuous flow method, when the rate of flow of water was 11 gm. per minute the heating current and potential difference between the ends of a wire were 2 amperes and 1 volt and the rise in temperature of the water was 2.5°C. On increasing the rate of flow to 25.4 gm/minute, the heating current to 3 amperes and P.D to 1.51 volts the rise to temperature was still the same. Determine the value of J .

$$V = 1 \text{ volt and } V' = 1.51 \text{ volts}$$

$$I = 2 \text{ Amp. and } I' = 3 \text{ Amp.}$$

$$m = 11 \text{ gms/minute and } m' = 25.4 \text{ gm/minute}$$

$$t_2 - t_1 = 2.5^\circ\text{C.}$$

Now

$$J = \frac{VI - V'I'}{S(m - m')(t_2 - t_1)}$$

$$= \frac{(1.51 \times 3 - 1 \times 2)}{(25.4 - 11)(2.5)} = 4.2 \text{ joules/cal.}$$

(4) **Callender's Brake Band Method.** A simple method of measuring J in the laboratory by a mechanical method was devised by Callendar and is shown in the Fig. 6.3.

The copper calorimeter which is in the form of a brass drum D contains a small quantity of water whose temperature is measured by thermometer A passing through a hole in the middle of D . A silk belt T is wound tightly round the drum, and a weight W_t (Mg) is attached to one end, while the other end of the silk belt is connected to the hook of a spring balance S . The drum is rotated at a

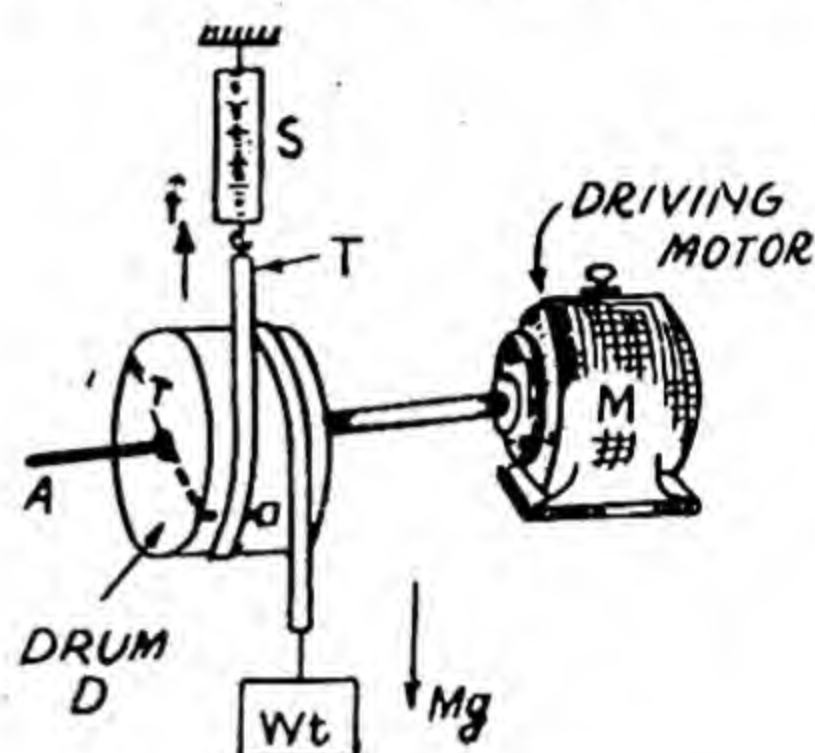


Fig. 6.3.

steady speed by an electric motor or by other mechanical means against the frictional force between silk belt T and the drum D . The number of revolutions described in a given time is determined from the reading on the revolution counter.

During the experiment the drum D is rotated at a steady speed, in this case the reading on S is fairly steady and W_t remains constantly in position. The silk belt also remains fixed in position, and work is therefore done against the frictional force between the belt and the drum by the motor. When a suitable rise in temperature is obtained the rotation of the drum is stopped and the true temperature rise is obtained.

Load on the silk belt	$T = W_t (Mg)$
Tension in spring balance	$S = f = m_1 g$
Water equivalent of drum	$= w$
Diameter of drum	$d = 2r$
Rise in temperature	$= t^\circ C$
No. of revolutions	$= n.$
mass of water in the drum	$= m.$
The frictional force	$F = Mg - f = Mg - m_1 g$ $= (M - m_1)g$

Note. 1. [The weight Mg acts downwards on the silk belt and the tension acts upward on the belt.]

Work done against friction = Force \times distance

$$\therefore \text{Work done } W = F \times 2\pi r n$$

Note 2. [In one revolution a point on the edge of the drum turns a distance $2\pi r$.]

$$\begin{aligned} \therefore \text{Work done} \quad W &= 2\pi r n (Mg - f) \\ &= 2\pi r n (Mg - m_1 g) \\ &= 2\pi r n (M - m_1) g \\ \text{Heat produced} \quad H &= (m + w) t \\ \therefore J &= \frac{W}{H} = \frac{2\pi r n (M - m_1) g}{(m + w) t} \\ &= \frac{2\pi r n g (M - m_1)}{(m + w) t} \text{ ergs/calorie} \end{aligned}$$

If W is measured in Joules and H in Kilo-cals, then J is measured in Joules/Kilo-cal.

The apparatus is used extensively in laboratories for demonstration and can give a reasonably accurate value of J provided the following precautions are observed.

(i) Correction should be applied for loss of heat due to radiation by taking the temperature of the water and cylinder in the beginning of the experiment as much below the room temperature as the final temperature will be above it.

(ii) The surface of the cylinder and the silk should be clean so that the friction is reasonably constant throughout the experiment.

(iii) Readings of the balance should be taken at intervals during the experiment, and if the drum is turned by hand, care should be exercised that the speed of rotation is constant.

Example 8. In a Callendar's experiment, the cylindrical copper calorimeter had a radius of 10 cms, a mass of 300 gms. and contained 150 gms of water. A silk band loaded with 3 kg. weight passed over its surface and when the drum was driven at a steady rate of 180 rev/mt. the average reading on the balance which was attached to the other end of the silk band was 560 gm. If the temperature of the water initially was 0°C and after 10 minutes running was 36°C , calculate the mechanical equivalent of heat. Specific heat of copper = 0.1.

Force of friction between the band and the drum

$$= (M - m)g = (3000 - 560) 981 \text{ dynes}$$

Distance covered in one revolution = $2\pi r$

$$= 2\pi \times 10 \text{ cms.}$$

Distance covered per minute = $180 \times 2\pi \times 10 \text{ cms.}$

\therefore Work done in 10 minutes = $(3000 - 560) 981 \times 180 \times 2\pi \times 10 \text{ ergs}$

Heat produced = $(m + w)t = (150 + 300 \times 0.1) 36 \text{ cals.}$

Now $W = JH$

$\therefore J = W/H$

$$= \frac{(3000 - 560) \times 981 \times 10 \times 180 \times 2\pi \times 10}{180 \times 36}$$

$$= 4.12 \times 10^7 \text{ ergs/cal.}$$

$$= 4.12 \text{ Joules/cal.}$$

(5) **Electrical method.** This method has already been discussed in the chapter on specific heat of liquids.

we know that

$$J = \frac{(VI - V'I')t}{S(m - m')(t_2 - t_1)}$$

If S the specific heat of liquid is known the value of J can be calculated.

(6) **Searle's Friction Cone Method.** A simple laboratory method in which heat is produced by friction between two metal cones is due to Searle. The apparatus is shown in the Fig. 6.4.

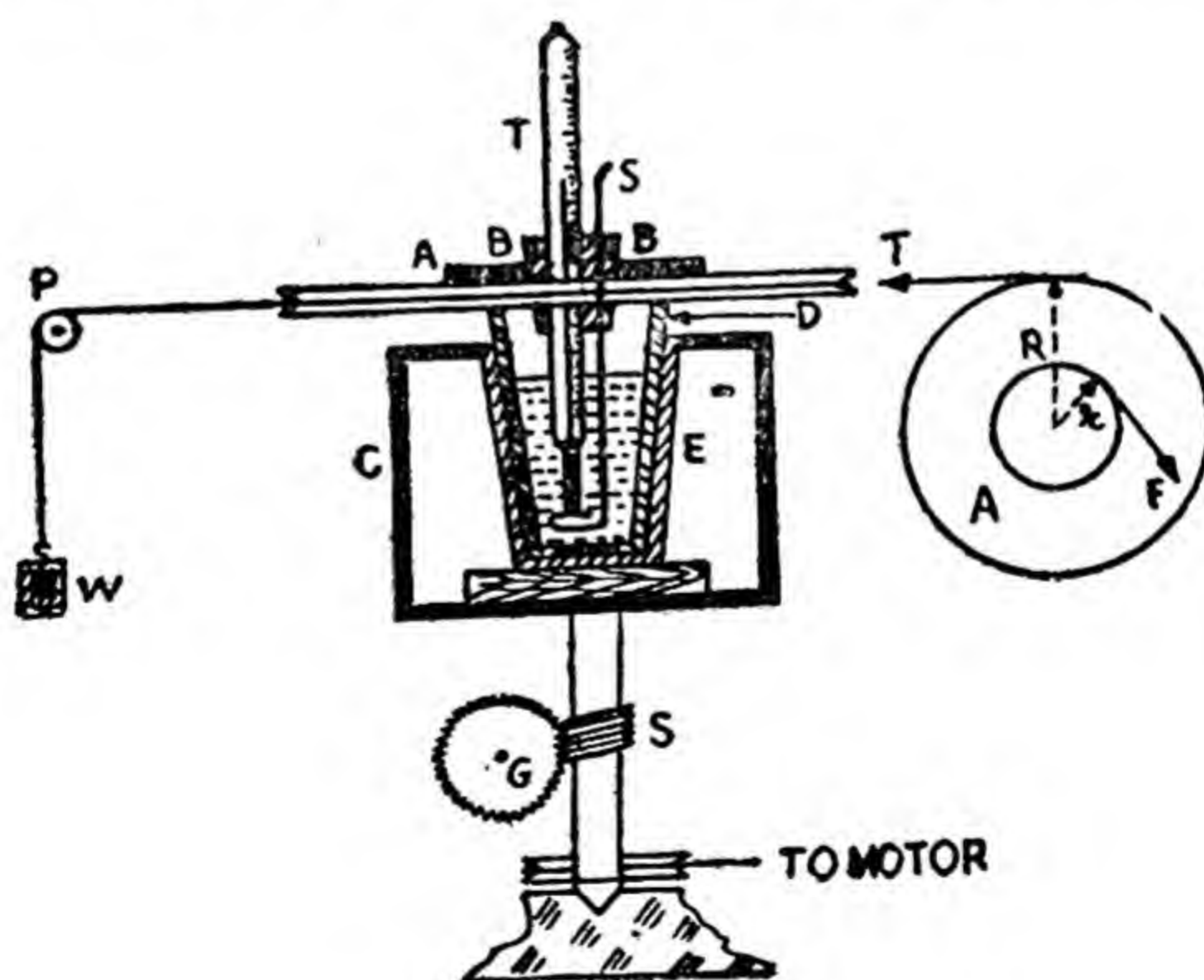


Fig. 6.4.

It consists of two truncated brass cones D and E fitting smoothly one inside the other. The inner cone D serves as a calorimeter and contains a known mass of water. A is a circular wooden disc which rests upon the inner cone D , to which it is attached by two sturdy pins. A leadweight B is placed on the top of the disc A to hold it in position. A string attached to the circumference of the disc passes over

a pulley P and is kept stretched by a known weight W fastened to its other end. The outer cone E is held rigidly in position by means of non-conducting ebonite pieces attached to the copper or brass cylinder C which is mounted on a spindle S and can be revolved by means of an electric motor or engine practically at a uniform speed. The counter G records the number of revolutions given to the cylinder C and hence to the outer cone. A sensitive thermometer T and a stirrer S are placed inside the inner cone as shown.

When the outer cone rotates rapidly the inner cone tends to move in the same direction on account of friction between the two. The continuous rotation of inner cone is prevented by applying the opposing couple provided by the weight W attached to the string passing round the disc D and over the pulley as shown. Now because of the friction which takes place between the surfaces in contact heat is produced which in turn heats the cones and water, placed in the inner cone. The amount of heat produced is determined from the knowledge of the water equivalent and the rise of temperature. The rise in temperature may be measured, with a sensitive thermometer T . A correction for the heat lost by radiation must also be applied.

The string must always be tangential to the circumference of the wooden disc when the apparatus is in use. The rotation of the spindle is so adjusted that the weight W remains practically stationary. In this position of equilibrium the moment due to the tension in the string is equal to the moment due to the frictional force. The number of revolutions made by the outer cone is recorded on the counter G .

Let R be the radius of the disc, and r the mean radius of the surface of contact of the cones. Then if F represent the mean value of frictional force between the cones.

$$F \times r = TR = MgR$$

Where M is the mass of the suspended load, g the acceleration due to gravity and T the tension in the string.

Since the frictional couple (Fr) applied by the rotating outer cone on the inner cone is equal and opposite to the couple applied by the weight Mg on cone D the work done in one revolution of the outer cone, assuming the inner cone to remain at rest $= F \times 2\pi r$.

When the outer cone makes n revolutions, the work done, W is given by

$$W = F \times 2\pi rn$$

Although the value of F and r separately cannot be determined accurately, the value of product Fr is given by MgR . Substituting this value, we find the mechanical work done

$$W = MgR \times 2\pi n$$

If t is the rise in temperature of water due to the heat produced by friction between the cones D and E , m the mass of water contained in the cone D , w the water equivalent of the cones A and B and stirrer,

then heat produced H due to friction is given by

$$H = (m + w)gt$$

$$\therefore J = \frac{W}{H} = \frac{Mg \times R \times 2\pi n}{(m + w)gt}$$

Example 9. Two brass cones fit one inside the other. The outer cone is rotated about a vertical axis at 600 r.p.m and the inner cone is held fixed by an arm whose length, measured from the axis of rotation, is 15 cm. and to which horizontal pull of 150 gm. wt. is applied at right angles to the arm. The total mass of the two cones together is 180 gms and the inner cone contains 25 gm. of water. Assuming that the initial temperature is 22°C and that there are no heat losses, find the temperature at the end of 5 minutes. The value of $J = 4.2$ joules/cal. and specific heat of brass $= 0.1$.

No. of revolutions made in 5 minutes

$$= 600 \times 5 = 3000$$

Force exerted $= 150$ gm. wt. $= 0.15$ kg. wt.

$$= 0.15 \times 9.81 \text{ Newtons}$$

The length of the arm from the axis of rotation $=$ the radius R of the disc $= 15$ cms $= 0.15$ metre

\therefore Work done against friction in 5 minutes

$$W = Mg \times 2\pi R \times n$$

$$= 0.15 \times 9.81 \times 2\pi \times 0.15 \times 3000 \text{ Joules}$$

$$= 4150 \text{ joules}$$

Hence heat produced $= \frac{4150}{4.2}$ calories

Water equivalent of the two cones

$$= 180 \times 0.1 = 18 \text{ gm.}$$

Effective wt. of water $m = 25 + 18 = 43$ gms.

If the rise of temperature is $t^\circ\text{C}$ then the heat produced is mSt where S is the specific heat of water taken to be unity.

$$\therefore 43 \times 1 \times t = \frac{4150}{4.2}$$

$$\text{or } t = \frac{4150}{4.2 \times 43} = 23^\circ\text{C}$$

$$\therefore \text{Final temperature is } = 22 + 23$$

$$= 45^\circ\text{C.}$$

Expected Questions

- (a) Discuss the significance of the expression that heat is a form of energy.
(b) What is meant by the term Mechanical Equivalent of Heat.
- Explain the superiority of Rowland's experiment over that of Joule's.
- Describe the Callendar and Barne's continuous flow method for the measurement of the mechanical equivalent of heat and point out the advantages of this method.
- Describe the Friction Cone method of determining the value of J and indicate the principles underlying this method.
- (a) Give in brief the brake band method for determining the value of J .
(b) Describe a simple electrical method for the determination of the value of J in the laboratory.

CHAPTER VII

EXPANSION AND COMPRESSION OF GASES

7.1. General gas energy temperature equation.

If heat is supplied to gases, in general there is a change in volume as well as temperature. Due to the increase of volume, work is done by the gases and a part of the heat energy supplied is converted into work which may be called as **external energy**. The remaining energy, is utilised to increase the temperature and is known as **internal energy**. Hence according to the law of conversation of energy,

Heat supplied = Gain of internal energy + External energy
(external work done)

$$\therefore dH = dE + \frac{dW}{J} \quad (i)$$

where J is the mechanical equivalent of heat.

The total heat of a substance is known as **enthalpy** which is measured by the equation (i) from a known condition. If the gas is cooled i.e., if the heat is rejected by the gas then H will be negative. Work done W will be negative if the gas is compressed.

7.2. Isothermal expansion of a gas. In a steam engine, the vapour expands at constant temperature in a cylinder during one stage of the action. The same type of gas expansion occurs at stages in gas engines. *When a change in pressure and volume of a gas takes place at constant temperature it is known as isothermal change.* (Iso-same, thermal-temperature). Mechanical engineer requires to study the laws governing the isothermal expansion and compression of a gas.

To understand how an isothermal change takes place consider a quantity of gas enclosed in a metal cylinder compressed by a piston. When the piston is *depressed* very slowly, mechanical work is done on the gas and some heat is produced. As the metal cylinder is a good conductor of heat, the heat produced escapes from the gas through the metal and the temperature remains constant. This is an example of an **isothermal change**.

Similarly, suppose that the piston in the cylinder is released very slowly, so that the gas expands. Work is done by the gas and the energy is taken from the gas itself, which therefore decreases slightly in temperature. If now heat is continuously supplied from outside through the metal cylinder so that temperature remains constant, the process is said to be an isothermal expansion.

Thus in an **isothermal** change the temperature is kept constant by adding heat or taking it away from the gas. For a perfect gas an isothermal change is represented by **Boyle's law** given by the equation,

$$PV = \text{constant}$$

The curve is a rectangular hyperbola as shown in the Fig. 7.1. As the PV diagram for an isothermal change, is a rectangular hyperbola, the process is also known as **hyperbolic process**.

Work done by a gas in isothermal expansion. Consider a unit mass of a perfect gas contained in an insulated cylinder and a perfectly conducting bottom fitted with a piston. If the piston is allowed to move slowly outwards the gas expands isothermally from an initial



Fig. 7.1.

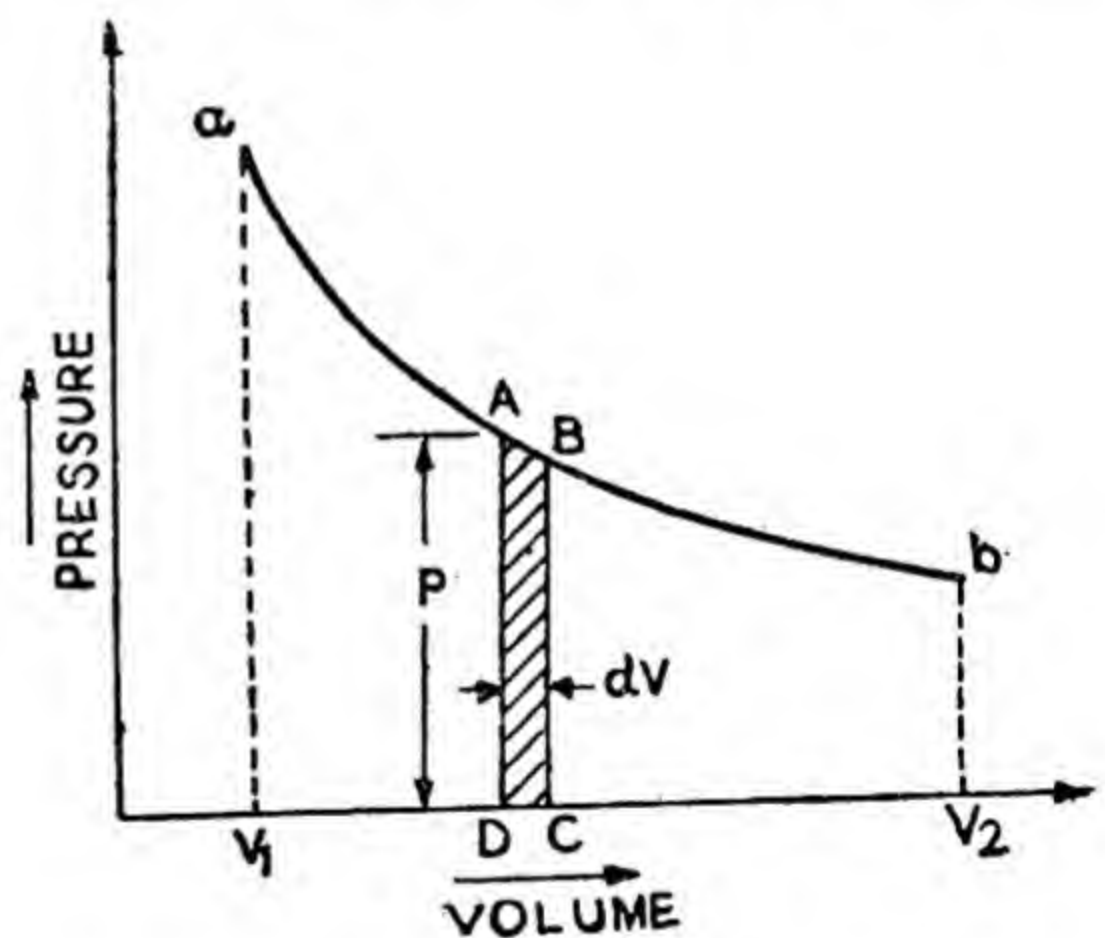


Fig. 7.2.

volume V_1 , and pressure P_1 (point a) to final volume V_2 and pressure P_2 (point b) as shown in the Fig. 7.2. The work done by the gas is given by the area abV_2V_1 . Consider some point A where the gas has a pressure P and a volume of V . Let the gas expand at this stage by a small amount $dV = (A \times dx)$. This increase in volume $dV = (A \times dx)$ is so small that the pressure P is supposed to remain constant during the small expansion. The work done by the gas during the small expansion is given by the area of the shaded vertical strip $AECD$ and is PdV .

$\therefore dW = P \times A \times dx$ where A = Area of cross-section of the piston and dx = small distance through which piston moves.

or

$$dW = PdV$$

But $PV = RT$

$$\therefore P = \frac{RT}{V}$$

Hence work done $dW = \frac{RT}{V} dV$.

Hence the total work done when the gas expands isothermally from volume V_1 to volume V_2 is given by

$$\int_0^W dW = RT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\therefore W = RT \log_e \frac{V_2}{V_1}$$

$$= RT \log_e r \quad \text{where } r = \text{ratio of expansion} = \frac{V_2}{V_1}$$

Further since $P_1 V_1 = P_2 V_2$

$$\therefore \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore W = RT \log_e \frac{V_2}{V_1} = RT \log_e \frac{P_1}{P_2}$$

$$\text{or} \quad = P_1 V_1 \log_e \frac{V_2}{V_1} = P_1 V_1 \log_e \frac{P_1}{P_2}$$

R represents gas constant for unit mass of the gas.

For one gm-mol of gas R should be substituted for R .

This work W is done due to the heat absorbed from the source. Hence heat absorbed from the source

$$H = \frac{W}{J} \text{ cals.}$$

where J is the mechanical equivalent of heat.

Examples of Isothermal operation. The following are the examples of the isothermal operations because temperature remains constant during their operations.

- (i) Fusion of solids at their melting point.
- (ii) Vaporisation of liquids at their boiling point.

Example 1. What is the pressure inside a motor tyre when 275 litres air is pumped into it at constant temperature and normal pressure. The internal volume of the tyre is 150 litres. (A.M.I.E)

Initial volume of air $V_1 = 275$ litres

Initial normal pressure $P_1 = 1$ atmosphere

Final volume of air $V_2 = 150$ litres

Final pressure of gas $P_2 = ?$

Now, for an isothermal process $PV = \text{constant}$

or $P_1 V_1 = P_2 V_2$

$$\therefore P_2 = \frac{P_1 \times 275}{150} = 1 \times \frac{11}{6} \\ = 1.83 \text{ atmospheres.}$$

Example 2. A gram molecule of a gas at 127°C expands isothermally until its volume is doubled. Find the amount of work done and heat absorbed. Given that mechanical equivalent of heat = 4.2 joules/calorie and $R = 8.3$ joules/gm. mole./ $^\circ\text{K}$.

The work done when a gas expands isothermally from the volume V_1 to V_2 at constant temperature T is given by the relation,

$$W = RT \log_e \frac{V_2}{V_1} \text{ for one gram-molecule of the gas.}$$

and $W = rT \log_e \frac{V_2}{V_1} \text{ for one gram of the gas.}$

where the symbols have their usual meanings.

Temperature $T = 273 + 127 = 400^\circ\text{K}$
 $R = 8.3$ joules/gm. molecule/ $^\circ\text{K}$

$$\frac{V_2}{V_1} = 2$$

$$W = RT \log_e \frac{V_2}{V_1} = 8.3 T \times 2.303 \log_{10} \frac{V_2}{V_1}$$

$$= 8.3 \times 400 \times 2.303 \log_{10} 2$$

$$= 8.3 \times 400 \times 2.303 \times 0.3010$$

$$= 2.3 \times 10^3 \text{ joules.}$$

Again heat absorbed $= \frac{W}{J} = \frac{2.3 \times 10^3}{4.2}$

$$= 548 \text{ calories.}$$

Example 3. Calculate the amount of work done when 10 cu. metre of air at a pressure of 2 kgm./sq.cm. and at a temperature of 20°C is compressed isothermally to a pressure of 10 kg./sq. cm. Also calculate the heat rejected during the process. and the change in internal energy.

Work done during the isothermal operation on the gas.

$$W = P_1 V_1 \log_e \frac{V_1}{V_2} = P_1 V_1 \log_e \frac{P_2}{P_1}$$

$$P_1 = 2 \times 10^4 \text{ kg./sq. m.}$$

$$V_1 = 10 \text{ cu. metre}$$

$$P_2 = 10 \times 10^4 \text{ kg./sq. m.}$$

$$\therefore \text{Work done} = 2 \times 10^4 \times 10 \log_e \frac{10 \times 10^4}{2 \times 10^4}$$

$$= 321,880 \text{ kg. metre}$$

As the temperature of the gas remains constant, so does the internal energy. Hence the change in internal energy is zero during the process.

$$\therefore \text{Heat rejected} = \text{Work done}$$

$$= \frac{321880}{J} = \frac{321880}{426.7}$$

$$= 754 \text{ k. cal.}$$

Where J is the mechanical equivalent of heat and is equal to 426.7 kg. metre/kilo calorie.

7.3. Adiabatic expansion of a gas. Besides undergoing isothermal changes, the gases in an engine expand and compress under such conditions that no heat **enters or leaves the gases**. The corresponding pressure volume changes are said to take place **adiabatically** and an adiabatic change is defined *as that change in which a change in pressure and volume of a gas take place under the condition that no heat is allowed to enter or leave it.*

We can understand how an adiabatic change can take place if we again consider a gas contained inside a cylinder fitted with a piston. But in this case the outside of the cylinder has been insulated and the piston is also made of insulating material. If the piston is depressed, **work is done on the gas**, and an equivalent amount of heat is produced. Unlike the case of an isothermal change however no heat escapes from the gas because the cylinder and piston are insulated and **with the result the temperature of the gas rises**. This is an example of an adiabatic compression. Thus during adiabatic compression work is done on the gas in compressing it as no heat leaves the gas during the process, its **internal energy** increases by an amount equal to the work done on it and consequently rise in temperature takes place.

If the piston is raised up the gas expands. Now the **work is done by the gas** and the equivalent of heat is taken from the gas itself, which is therefore cooled. No heat, however enters or leaves the gas while it expands, and this is the example of an adiabatic expansion. Thus during adiabatic expansion external work is done by the gas and as no heat is supplied to the gas from an external source during the process, its **internal energy** decreases by an amount equal to the work done by the gas and consequently a fall in temperature takes place.

Hence in the example given above if no heat is taken away in the first case the temperature will rise and if no heat is supplied in the second case the temperature will fall. Hence in an adiabatic change the temperature does not remain constant and no heat from outside is supplied to the system or taken from it.

Hence in an adiabatic change.

- (i) No heat enters or leaves the gas *i.e.*, $H=0$
- (ii) But temperature changes as the work is done at the expense of internal energy.
- (iii) Change in internal energy *i.e.*, increase or decrease in the internal energy of the gas is exactly equal to the work done on or by the gas.

∴ From energy gas equation we have for a perfect gas,

$$0 = E + \frac{W}{J}$$

7.4. Derivation of adiabatic equation of a gas.

Consider m gms of a perfect gas contained in a perfectly insulated cylinder fitted with an insulating piston. Let its pressure, volume and temperature be P, V and T respectively. Suppose the gas is compressed adiabatically so that piston moves inwards through a distance dx . If A is the area of cross-section of the piston the total force applied is $P \times A$ and work done by the piston

$$\begin{aligned} &= \text{Force} \times \text{distance} = P \times A \times dx \\ &= P \times (A dx) \\ &= P \times dV \end{aligned}$$

where $A dx = dV$ gives the change in volume. The heat produced due to compression causes a rise of temperature dT and is given by $mC_v dT$ where C_v is the specific heat of gas at constant volume.

Hence increase in internal energy $dE = mC_v dT$.

As no heat has been supplied from outside,

We have $dH = 0$

∴ General gas energy equation becomes,

$$dE + \frac{dW}{J} = 0$$

$$\text{or } mC_v dT + \frac{PdV}{J} = 0 \quad \dots(i)$$

Now for a perfect gas

$$PV = R_0 T \quad \dots(ii)$$

where $R_0 = mR$

Differentiating (ii), we have

$$\begin{aligned} PdV + VdP &= mRdT \\ \therefore dT &= \frac{PdV + VdP}{mR} \end{aligned}$$

Substituting the value of dT in (i), we have

$$mC_v \frac{PdV + VdP}{mR} + \frac{PdV}{J} = 0$$

or $C_v \frac{PdV + VdP}{R} + \frac{PdV}{J} = 0$

$$(C_v PdV + C_v VdP) J + R PdV = 0$$

or $(C_v J + R) PdV + C_v JVdP = 0$

But $C_p - C_v = \frac{R}{J}$

or $C_p J = (R + C_v J)$

$\therefore C_p J PdV + C_v JVdP = 0$

or $C_p PdV + C_v VdP = 0$

Dividing by $C_v PV$ and putting $\frac{C_p}{C_v} = \gamma$, we have

$$C_p \frac{PdV}{C_v PV} + \frac{C_v VdP}{C_v PV} = 0$$

or $\frac{C_p}{C_v} \frac{dV}{V} + \frac{dP}{P} = 0$

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0$$

Integrating both sides we get,

$$\gamma \log_e V + \log_e P = \text{constant}$$

$$\log_e V^\gamma + \log_e P = \text{constant}$$

or $\log_e PV^\gamma = \text{constant}$

or $PV^\gamma = \text{constant}$

It is known as an adiabatic equation of a perfect gas. In other words if P_1, V_1 are the initial and P_2, V_2 the final pressures and volumes of the gas for an adiabatic change, then

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

or $\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma$

According to the perfect gases equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or $\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$

Substituting for $\frac{P_2}{P_1}$ in the above relation from the adiabatic gas

equation, we get

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^\gamma \frac{V_2}{V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\text{i.e. } TV^{\gamma-1} = \text{Constant}$$

Again from the same equation

$$\frac{V_1}{V_2} = \left(\frac{P_2}{P_1}\right)^{\frac{1}{\gamma}}$$

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\therefore \frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

$$\text{or } \left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_2}{P_1}\right)^{\gamma-1}$$

$$\therefore \frac{T^\gamma}{P^{\gamma-1}} = \text{Constant}$$

Hence the three forms of an adiabatic gas equation are

$$PV^\gamma = \text{Constant}$$

$$TV^{\gamma-1} = \text{Constant}$$

$$\frac{T^\gamma}{P^{\gamma-1}} = \text{Constant}$$

Now from the equation

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

Imp.

7.5. Adiabatic curves are steeper than Isothermal curves.
The isothermal equation $PV = \text{constant}$ and the adiabatic equation

$PV^\gamma = \text{constant}$ have been plotted as shown in the Fig. 7.3. Let us consider a point P on the PV curves which represents a given mass of gas under conditions of pressure, volume and temperature P , V and T . Now it will be shown that the slope of the adiabatic curve is greater than the slope of the isothermal curve.

The slope of any curve on the PV diagram is given by $\frac{dP}{dV}$.

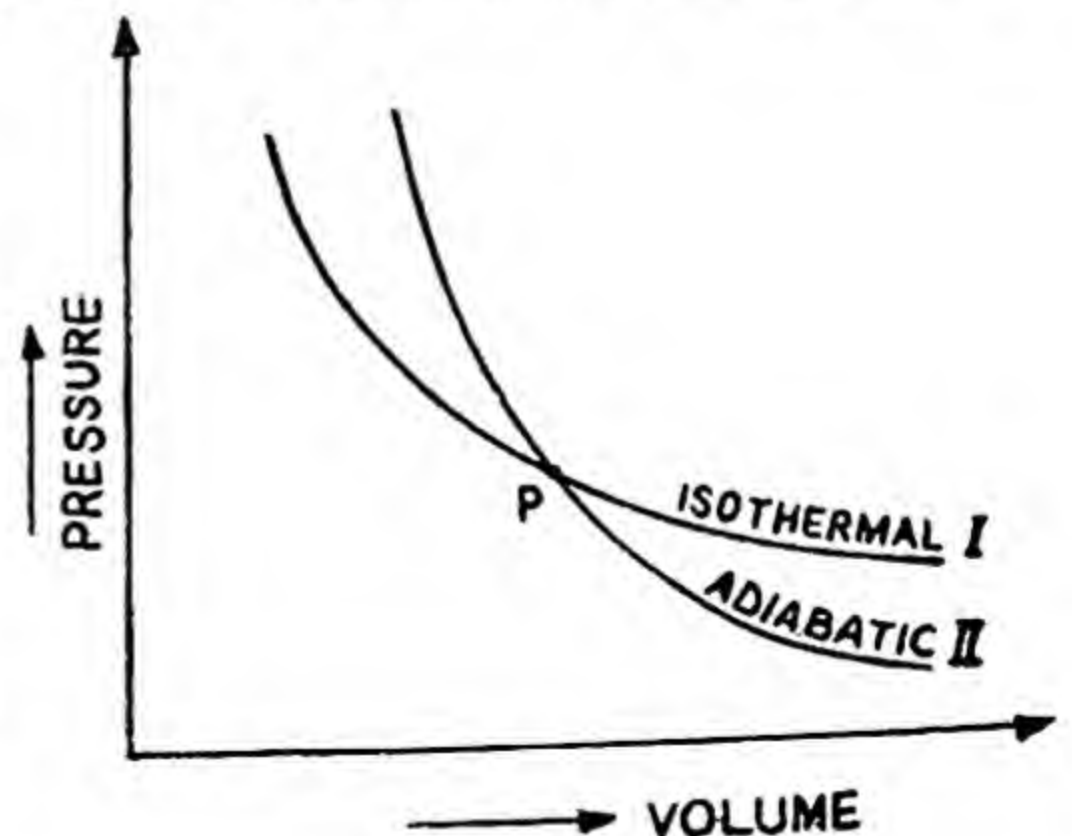


Fig. 7.3

Case 1. Isothermal curve I.

For an isothermal curve

$$PV = \text{constant}$$

$$\therefore PdV + VdP = 0$$

By partial differentiation, we get

$$\text{or} \quad \frac{dP}{dV} = -\frac{P}{V} \quad \dots(i).$$

Case 2. Adiabatic curve II.

For adiabatic curve

$$PV^\gamma = \text{constant}$$

$$\gamma PV^{\gamma-1} dV + V^\gamma dP = 0$$

$$\therefore \gamma PdV + VdP = 0$$

$$\text{or} \quad \frac{dP}{dV} = -\gamma \frac{P}{V}$$

$$= \gamma \times \text{isothermal slope.}$$

Since γ is always greater than unity therefore the slope of the adiabatic curve is always greater (steeper) than that of the isothermal.

7.6. Work done by a gas during adiabatic expansion. Consider m gm. of a perfect gas contained in a perfectly insulated cylinder. Let V be the volume P the pressure and $T^\circ K$ the temperature of the gas. If the piston is allowed to move suddenly outward the gas expands and does some work. Since no heat is supplied from outside, the change is **adiabatic** and the internal energy is drawn from the gas due to which the temperature of the gas falls.

If A is the area of cross-section of the piston and it moves through a small distance dx , then the work done for a small change in volume as shown in Fig. 7.2 is given by

$$\begin{aligned} \text{Work done} &= dW = P \times A \times dx \\ &= P \times (A dx) = PdV \end{aligned}$$

Since, the expansion is adiabatic,

$$\therefore PV^\gamma = K$$

$$\text{or} \quad P = \frac{K}{V^\gamma}$$

$$\therefore dW = K \frac{dV}{V^\gamma}$$

Hence the total work done when the gas expands adiabatically from the volume V_1 to the volume V_2 is given by.

$$\int_{V_1}^{V_2} dW = K \int_{V_1}^{V_2} \frac{dV}{V^\gamma}$$

$$\begin{aligned}
 \text{or } W &= \frac{K}{1-\gamma} \left[V^{1-\gamma} \right]_{V_1}^{V_2} \\
 &= \frac{K}{1-\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right] \\
 &= \frac{1}{\gamma-1} \left[\frac{K}{V_1^{\gamma-1}} - \frac{K}{V_2^{\gamma-1}} \right]
 \end{aligned}$$

Now $P_1 V_1^\gamma = P_2 V_2^\gamma = K$.

$$\begin{aligned}
 \therefore W &= \frac{1}{1-\gamma} \left[\frac{P_1 V_1^\gamma}{V_1^{\gamma-1}} - \frac{P_2 V_2^\gamma}{V_2^{\gamma-1}} \right] \\
 &= \frac{1}{1-\gamma} (P_1 V_1 - P_2 V_2)
 \end{aligned}$$

This expression gives the work done by a gas during an adiabatic expansion in terms of initial and final pressures and volumes. The same can be expressed in terms of initial and final temperatures and the characteristic gas constant R as given below,

$$\begin{aligned}
 P_1 V_1 &= m R T_1 \text{ and } P_2 V_2 = m R T_2 \\
 \text{or } P_1 V_1 - P_2 V_2 &= m R (T_1 - T_2) \\
 \therefore W &= \frac{m R (T_1 - T_2)}{\gamma - 1}
 \end{aligned}$$

If one gm. mol. of a gas is considered, then

$$W = \frac{M R (T_1 - T_2)}{\gamma - 1}$$

This shows that the work done during an adiabatic expansion is proportional to the fall in temperature. On the other hand if there is an adiabatic compression the temperature of the gas will increase which is proportional to the work done on the gas.

Examples of adiabatic operations.

(i) A sudden compression of air in a bicycle pump, because no heat leaves the air when compression takes place and its temperature rises.

(ii) The condensations and rarefactions in sound waves in air are examples of perfectly adiabatic operations.

Example. 4. Dry air at normal pressure and at 27°C is compressed to one third of its original volume under adiabatic conditions. Determine the resultant pressure when $\gamma = 1.4$.

Initial pressure of the gas $P_1 = 1$ atmosphere.

Initial volume $V_1 = V$

Final volume $V_2 = \frac{V}{3}$ and $\gamma = 1.4$.

Final pressure $P_2 = ?$

But $PV^\gamma = \text{constant}$

$\therefore P_1 V_1^\gamma = P_2 V_2^\gamma$

or $1. V_2 = P_2 \left(\frac{V}{3} \right)^\gamma$

or $P_2 = V^\gamma \left(\frac{3}{V} \right)^\gamma = V^\gamma (3)^\gamma V^{-\gamma} = (3)^\gamma = (3)^{1.4}$

$= 4.655 \text{ Atmospheres}$

Example 5. Calculate the rise in temperature when a gas is compressed to 8 times its original pressure, assuming that initial temperature is 27°C .

Initial pressure $P_1 = P$

Final pressure $P_2 = 8P$

Initial temperature $T_1 = 273 + 27 = 300^\circ\text{K}$

Final temperature $T_2 = ?$

we know that $\frac{P^{\gamma-1}}{T^\gamma} = \text{constant.}$

$\therefore P_1^{\gamma-1} T_1^{-\gamma} = P_2^{\gamma-1} T_2^{-\gamma}$

or $\left(\frac{T_2}{T_1} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{\gamma-1}$

$\therefore \left(\frac{T_2}{300} \right)^{1.5} = \left(\frac{8P}{P} \right)^{1.5-1} = (8)^{0.5}$

or $\frac{(T_2)^{1.5}}{(300)^{1.5}} = 8^{0.5}$

or $T_2 = \left[(300)^{1.5} \times 8^{0.5} \right]^{\frac{1}{1.5}} = 599.8^\circ\text{K.}$

[These calculations have been done on slide rules.]

\therefore Temperature $t_2 = 599.8 - 273 = 326.8^\circ\text{C}$

Hence rise in temperature $= 326.8^\circ - 27$
 $= 299.8^\circ\text{C}$

Example 6. A quantity of air at N.T.P. is suddenly compressed $\frac{1}{5}$ th of its volume. Calculate the temperature attained by air when $\gamma = 1.40$.

Initial volume $V_1 = V$ say,

Final volume $V_2 = \frac{1}{5}V$

Initial temperature $T_1 = 273 + 0$

Final temperature $T_2 = ?$ and $\gamma = 1.40$.

For an adiabatic change $TV^{\gamma-1} = \text{constant}$

$$\therefore T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} = (5)^{\gamma-1} = 5^{0.4}$$

$$\text{or } \log T_2 - \log T_1 = 0.4 \log 5$$

$$\log T_2 - \log 273 = 0.4 \log 5$$

$$\therefore \log T_2 = 0.4 \log 5 - \log 273 = 2.7188$$

$$\text{Hence } T_2 = 519.8^\circ K$$

$$\therefore \text{Rise in temperature} = 519.8 - 273 \\ = 246.8^\circ C$$

Example 7. A certain quantity of air ($\gamma = 1.4$) at N.T.P. is adiabatically compressed to $\frac{1}{4}$ th of its original volume. Find the resulting temperature and pressure. (A.M.I.E.)

Let original volume be equal to V_1

$$T_1 = 273^\circ K$$

$$P_1 = 76 \text{ cms of mercury}$$

$$\text{Now } V_2 = \frac{1}{4} \text{ of its original volume} = \frac{1}{4} V_1.$$

$$T_2 = ? \quad \text{and } P_2 = ?$$

$$\text{Applying } T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \text{ we have}$$

$$\text{or } T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$= 273 \left(\frac{1}{\frac{1}{4}} \right)^{0.4} = 273 \times 1.74$$

$$= 475^\circ K.$$

$$= 202^\circ C.$$

$$\text{Now applying } P_1 V_1^\gamma = P_2 V_2^\gamma, \text{ we have}$$

$$\begin{aligned} \text{or} \quad P_2 &= P_1 \left(\frac{V_1}{V_2} \right)^\gamma = 76 (4)^{1.4} \\ &= 76 \times 6.965 \\ &= 529.3 \text{ cms. of Mercury} \end{aligned}$$

Example 8. One Kg. of air is at a pressure and temperature of 7 atmosphere and 100°C respectively. Find its volume and its internal energy reckoning internal energy as zero in the standard state. The air is allowed to expand to 4 times its initial volume adiabatically, determine the pressure, temperature and internal energy.

According to the gas equation,

$$\therefore PV = RT \quad (i)$$

If P is in Kg/sq met. V in cubic metres, T in degree Absolute, then R is in Kilo-cal/Kgm/ $^\circ\text{K}$.

$$\begin{aligned} P &= 7 \times 10^4 \text{ kg/sq.M.} & R &= 29.27 \text{ K. Cal./kg/}^\circ\text{K.} \\ T &= 273 + 100 & &= 373^\circ\text{K.} \end{aligned}$$

Substituting in (i) we have

$$7 \times 10^4 \times V = 29.27 \times 373$$

$$\therefore V = \frac{29.27 \times 373}{7 \times 10^4} = 0.156 \text{ cubic metre.}$$

$$\begin{aligned} \text{Internal energy of 1 kg. of air} &= C_v \times 1 \times \text{change in temperature} \\ &= 0.171 \times 1 \times (373 - 273) \\ &= 0.171 \times 1 \times 100 = 17.1 \text{ k. cal./kg.} \end{aligned}$$

Now for adiabatic expansion $PV^\gamma = \text{constant}$

$$\therefore P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\text{where } P_1 = 7 \times 10^4 \text{ kg/sq.M.} = P_2 = ?$$

$$V_1 = V_1 \text{ cubic metre} \quad V_2 = 4V_1 \text{ cubic metre}$$

and

$$\gamma = 1.4.$$

$$\therefore 7 \times 10^4 (V_1)^{1.4} = P_2 (4V_1)^{1.4}.$$

$$\text{or } P_2 = \frac{7 \times 10^4}{4^{1.4}} = 10050 \text{ kg/sq.M.}$$

$$\text{As } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \text{ we get}$$

$$\frac{7 \times 10^4 V_1}{373} = \frac{10050 \times 4V_1}{T_2}$$

$$\text{or } T_2 = 373 \times \frac{10050}{7 \times 10^4} \times \frac{4V_1}{V_1} = 214.2^\circ\text{K.}$$

$$t_2 = 214.2 - 273 = -58.8^\circ\text{C.}$$

$$\begin{aligned} \text{Internal energy} &= C_v \times 1 \times (\text{change in temperature}) \\ &= 0.171 \times 1 (214.2 - 273) \\ &= 0.171 \times 1 \times (-58.8) \\ &= -12.055 \text{ k. cal.} \end{aligned}$$

Example 9. One kg. of a gas expands adiabatically and its temperature is observed to fall from 240°C to 115°C while the volume is doubled. The gas does 9160 kg. metres of work in the process. Determine the values of C_p and C_v .

Work done by the gas 9160 kg. metres

$$= \frac{9160}{426.7} \text{ Kilo-cal.}$$

$$= 21.48 \text{ kilo. cal./kg.}$$

Work done during adiabatic operation is numerically equal to change in internal energy.

Change in internal energy per kg.

$$= C_v (T_1 - T_2)$$

$$\therefore 21.48 = C_v (273 + 240) - (273 + 115)$$

$$= C_v (513 - 388)$$

$$= C_v 125$$

$$\therefore C_v = \frac{21.48}{125} = 0.0172$$

Again $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

where

$$V_2 = 2V_1$$

$$\frac{513}{388} = (2)^{\gamma-1}$$

$$\therefore \gamma = 1.4$$

$$C_p = \gamma C_v = 1.4 \times 0.0172$$

$$= 0.02408$$

Example 10. A cylinder containing one-gram molecule of the gas was put on boiling water bath and allowed to expand adiabatically until its temperature rose from 27°C to 97°C . Calculate the work done and heat absorbed by the gas ($\gamma = 1.5$). Take $J = 4.2$ joules/cal.

Work done during adiabatic expansion when the temperature changes from T_1 to T_2 is given by the relation

$$W = \frac{R}{\gamma-1} (T_1 - T_2)$$

Where R is the gas constant for one gm. molecule of the gas, γ is the ratio of the specific heat at constant pressure to the specific heat at constant volume.

Now

$$T_1 = 273 + 27 = 300^{\circ}\text{K}$$

and

$$T_2 = 273 + 97 = 370^{\circ}\text{K}$$

$$\therefore W = \frac{R}{\gamma-1} (T_1 - T_2)$$

$$= \frac{8.3 (370 - 300)}{1.5 - 1} = \frac{8.3 \times 70}{0.5}$$

$$= 11.62 \times 10^2 \text{ joules.}$$

$$\text{Heat absorbed} = \frac{W}{J} = \frac{11.62 \times 10^2}{4.2}$$

$$= 276.6 \text{ cal.}$$

Example 11. 5 cubic ft. of air ($\gamma = 1.41$) under a pressure of 89.7 pounds per sq. inch is expanded adiabatically to 39.7 pounds per sq. inch absolute. Find the work done during expansion. (A.M.I.E.)

The work done during adiabatic expansion is given by

$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

Also $PV^\gamma = \text{constant}$

or $P_1 V_1^\gamma = P_2 V_2^\gamma$

Now

$$P_1 = 89.7 \text{ pounds per sq. inch}$$

$$P_2 = 39.7 \text{ pounds per sq. inch}$$

$$\gamma = 1.41$$

$$V_1 = 5 \text{ cu. ft.}$$

and

$$V_2 = ?$$

$$\therefore \left(\frac{V_2}{V_1} \right)^\gamma = \frac{P_1}{P_2}$$

or $\frac{V_2}{V_1} = \left(\frac{P_1}{P_2} \right)^{\frac{1}{\gamma}}$

or $V_2 = V_1 \left(\frac{P_1}{P_2} \right)^{\frac{1}{\gamma}}$

$$= 5 \left(\frac{89.7}{39.7} \right)^{\frac{1}{1.41}}$$

$$= 8.91 \text{ cu. ft.}$$

$$\therefore \text{Work done} = \frac{(89.7 \times 144 \times 5 - 39.7 \times 144 \times 8.91)}{1.41 - 1}$$

$$= 33000 \text{ ft. lb.}$$

Example 12. One kg. of air expands adiabatically through a volume ratio of 5 : 1. The initial pressure and temperature are 28 atm. and 220°C respectively. Find (i) the final pressure and temperature and (ii) the work done during expansion. For air $C_p = 0.245$ and $C_v = 0.175$.

Here $P_1 = 28 \times 10^4$ Kg./sq. metre.
 $V_1 = V_1$ cubic metre

$P_2 = ?$
 $V_2 = 5V_1$
 $C_p = 0.245$
 $C_v = 0.175$

$$\gamma = \frac{C_p}{C_v} = \frac{0.245}{0.175} = 1.4$$

Now for an adiabatic change $P_1 V_1^\gamma = P_2 V_2^\gamma$

$$\text{or } 28 \times 10^4 \times V_1^{1.4} = P_2 (5 V_1)^{1.4}$$

$$\therefore P_2 = \frac{28 \times 10^4}{5^{1.4}} = 2.95 \times 10^4 \text{ kg./sq. metre or technical atmosphere}$$

Now by applying the gas equation

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}, \text{ we have}$$

$$\frac{28 \times 10^4 V_1}{T_1} = \frac{2.95 \times 5 V_1}{T_2}$$

$$\text{But } T_1 = 220 + 273 = 493^\circ \text{K.}$$

$$\therefore \frac{28 \times 10^4 \times V_1}{493} = \frac{2.95 \times 10^4 \times 5 V_1}{T_2}$$

$$T_2 = 493 \times \frac{2.95 \times 10^4}{28 \times 10^4} \times 5 = 259^\circ \text{K}$$

$$\therefore t_2 = 259 - 273 = -14^\circ \text{C.}$$

$$\text{Also } R = (C_p - C_v) J = (0.245 - 0.175) 426.7 \\ = 29.87 \text{ Kg. metre/kg./}^\circ \text{K.}$$

$$\text{Work done during the expansion per kg.} = \frac{R (T_1 - T_2)}{\gamma - 1}$$

$$= \frac{29.87 (493 - 259)}{1.4 - 1}$$

$$= 17,470 \text{ kg. metre.}$$

Example 13. A mass of a gas at 80°C and 50 atmosphere pressure is adiabatically expanded to ten times its initial volume. If the ratio of the specific heats is 1.4, calculate the resulting pressure and temperature.

If the total mass of the gas is a gm. molecule, calculate the work done in the process. The universal gas constant is 2 calories. (A.M.I.E)

Before Expansion

$$P_1 = 50 \text{ atmospheres, } T_1 = 273 + 80 = 353^\circ \text{K, and volume} = V_1$$

After Expansion.

$$P_2 = ?, T_2 = ?, \text{ and } V_2 = 10V_1 \text{ and } \gamma = 1.4$$

Now applying adiabatic expansion equation, we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\therefore T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 353 \left(\frac{V_1}{10V_1} \right)^{1.4-1} = 353 \times 10^{-0.4} = 140.6^\circ K$$

$$\therefore \text{Temperature} = 140.6 - 273 = -132.4^\circ C$$

$$\text{Also } P_1 V_1^{\gamma-1} = P_2 V_2^{\gamma}$$

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^{\gamma} = 50 \left(\frac{V_1}{10V_2} \right)^{1.4} = 50.10^{-1.4} = 1.99 \text{ atmospheres}$$

For one gm-mol of the gas, the equation for work done is given as.

$$\begin{aligned} W &= \frac{R(T_1 - T_2)}{\gamma - 1} \text{ cal.} \\ &= \frac{2(353 - 140.6)}{1.4 - 1} = 1062 \text{ cal.} \end{aligned}$$

Example 14. A certain volume of dry air at S.T.P. is expanded to 3 times its volume under (a) isothermal conditions (b) adiabatic conditions. Calculate in each case the final pressure and temperature $\gamma = 1.4$ for air.

The abbreviation S.T.P. means, standard temperature and pressure i.e. temperature of $0^\circ C = 273^\circ K$ and pressure 1 atmosphere or 76 cms. of mercury. Let V_1 be the volume of dry air at S.T.P.

(a) **Isothermal Conditions.**

$$\text{Initial pressure } P_1 = 76 \text{ cms.}$$

$$\text{Initial volume } V_1 = V_1$$

$$\text{Final volume } V_2 = 3 V_1$$

$$\text{Final pressure } P_2 = ?$$

$$\therefore P_1 V_1 = P_2 V_2$$

$$\text{or } P_2 = \frac{P_1 V_1}{V_2} = \frac{76 \times V_1}{3V_1} = 25.33 \text{ cms. of Hg}$$

Under Isothermal conditions there is no change in temperature.

(b) **Adiabatic Conditions.**

For an adiabatic change,

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$\text{or } P_2 = P_1 \left(\frac{V_1}{V_2} \right)^{\gamma} = 76 \left(\frac{V_1}{3V_1} \right)^{1.4}$$

$$\therefore \text{Pressure } P_2 = \frac{76}{(3)^{1.4}} = 16.32 \text{ cms.}$$

$$\text{Also } T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\text{Here } T_1 = 273^\circ K$$

$$\therefore 273 V_1^{\gamma-1} = T_2 (3 V_2)^{\gamma-1}$$

$$\begin{aligned} \text{or } T_2 &= 273 \left[\frac{V_1}{3V_2} \right]^{\gamma-1} \\ &= 273 \frac{1}{(3)^{\gamma-1}} = \frac{273}{3^{0.4}} = 176.0^\circ K. \end{aligned}$$

$$\therefore \text{Temperature} = 273 - 176 = 97^\circ C$$

7.7. Compressibility of a gas. Consider a gas having volume V , under a pressure P , and subject it to a small increase of pressure dP . The volume will be reduced to $V - dV$ then

$$\text{volume strain} = \frac{\text{Change in volume}}{\text{Original volume}} = \frac{-dV}{V}$$

$$\text{and stress} = \text{Applied force/unit area} = dP$$

$$\text{Hence Elasticity } E = \frac{\text{Stress}}{\text{Strain}} = \frac{dP}{-\frac{dV}{V}} = -V \frac{dP}{dV}$$

The value of the elasticity depends upon the conditions under which the compression takes place. Under isothermal conditions it is known as *Isothermal Elasticity* (E_{iso}) and for adiabatic conditions it is known as *Adiabatic Elasticity* (E_{adi}).

The compressibility K of a gas is the reciprocal of the volume elasticity and is defined as the fractional decrease in volume per unit increase in pressure.

$$\text{i.e., } K = \frac{1}{E} = -\frac{dV}{V} \times \frac{1}{P} = \text{compressibility}$$

$$\text{Isothermal compressibility} = K_{iso} = \frac{1}{E_{iso}}$$

$$\text{and adiabatic compressibility} = K_{adi} = \frac{1}{E_{adi}}$$

We can obtain the values of E_{iso} (K_{iso}) and E_{adi} (K_{adi}) from the gas laws.

(a) **Isothermal conditions.** The isothermal equation of the gas is $PV = \text{constant}$

Differentiating w. r. t. V , we have

$$P + V \frac{dP}{dV} = 0$$

$$\therefore -V \frac{dP}{dV} = P$$

But $E = -V \frac{dP}{dV}$

$$\therefore E_{iso} = P$$

But $K_{iso} = \frac{1}{E_{iso}} = \frac{1}{P}$

Hence isothermal compressibility of a gas is equal to the reciprocal of its pressure P .

(b) **Adiabatic conditions.** The adiabatic equation of a gas is

$$PV^\gamma = \text{constant.}$$

Differentiating w.r.t. V , we have

$$P\gamma V^{\gamma-1} + V^\gamma \frac{dP}{dV} = 0$$

$$P\gamma V^{\gamma-1} + V V^{\gamma-1} \frac{dP}{dV} = 0$$

or $P\gamma + V \frac{dP}{dV} = 0$

or $-V \frac{dP}{dV} = \gamma P$

But $E = -V \frac{dP}{dV}$

$$\therefore E_{adi} = \gamma P$$

$$\therefore K_{adi} = \frac{1}{E_{adi}} = \frac{1}{\gamma P}$$

$$K_{adi} = \frac{1}{\gamma} \times K_{iso}$$

\therefore Adiabatic compressibility

$$= \frac{1}{\gamma} \times \text{Isothermal compressibility}$$

Also $\frac{K_{iso}}{K_{adia}} = \frac{E_{adi}}{E_{iso}} = \gamma = \frac{C_p}{C_v}$ ratio of two specific heats.

7.8. Clement and Desorme's Method for the determination of $\gamma \left(\frac{C_p}{C_v} \right)$. In

1819 Clement and Desorme's designed a simple method of measuring γ , the ratio of the two specific heats of a gas. The apparatus consists of a big, thick walled glass flask placed in a wooden box packed with saw dust, cotton wool or some other insulating material to avoid heat losses. The mouth of the flask is closed by a tight-fitting rubber stopper through a tight tap T from where connections are taken to (i) a pump, (ii) a monometer using light oil or sulphuric acid and (iii) a wide bore stop cock S . The flask is filled with the dry gas at a pressure greater than the atmospheric pressure P , and the stop cock S is closed. In order to completely dry the gas inside the flask some strong sulphuric acid is kept in the flask. After some time when the enclosed gas attains room temperature, the manometer reading is taken. The pressure P_1 is calculated from the equation

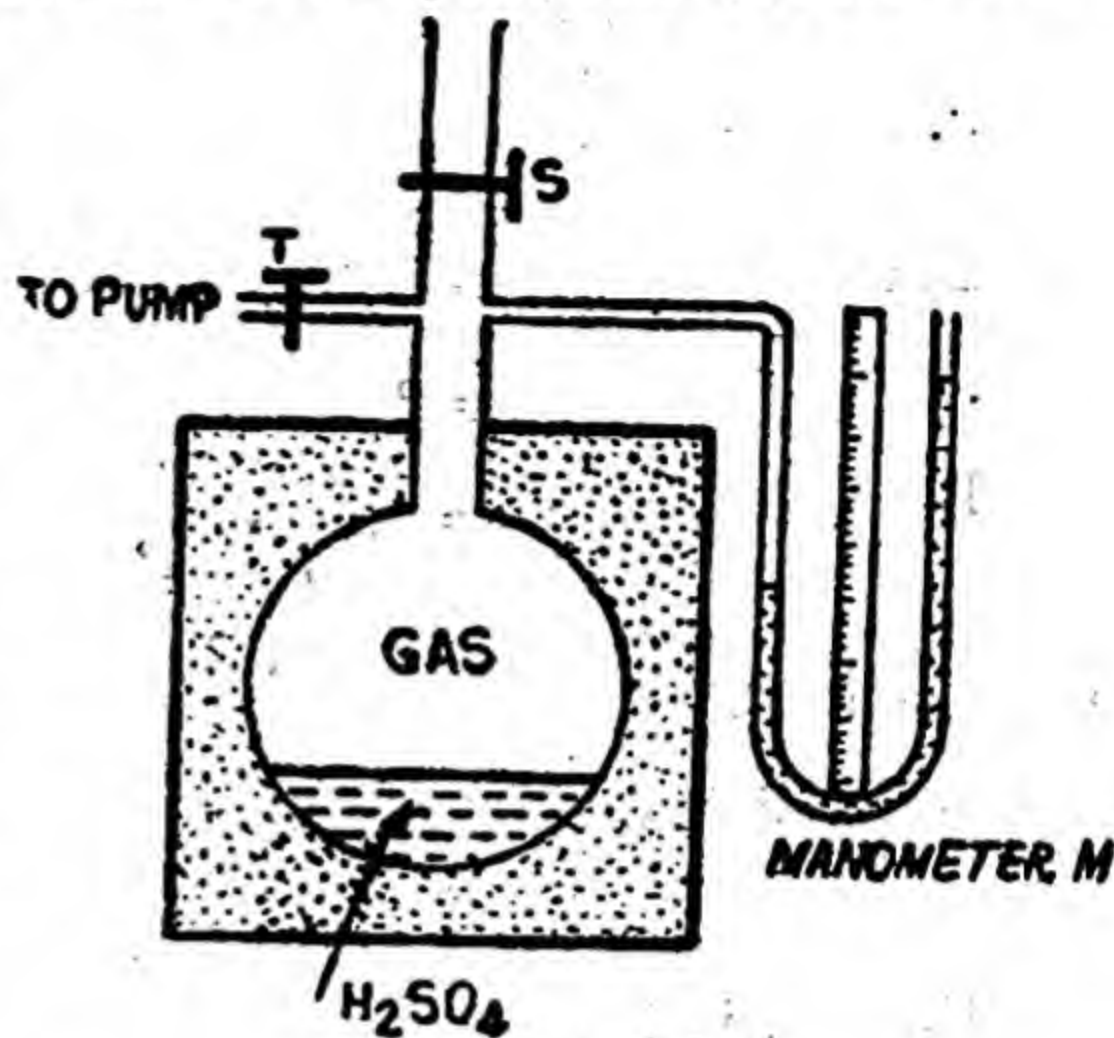


Fig. 7.4

Where P = atmospheric pressure, in cms. of Hg, ρ the density of the oil, D the density of the mercury and h_1 the reading of the manometer.

The stop cock S is opened quickly for a few seconds and closed. During the time the stop cock S remains open the gas in the flask rushes out to equalize the pressure and just when the stop cock is closed the gas inside it is at the atmospheric pressure. As the flask is completely insulated no heat is either gained or lost and the process is **adiabatic**. Thus during the expansion of the gas under adiabatic conditions the temperature falls. The apparatus is then left in this condition for some time to allow the enclosed gas which was cooled in the adiabatic expansion to regain room temperature. This causes an increase in pressure to P_2 , and apart from a slight change in volume due to the movement of the liquid in the manometer, which is negligible, the volume of the gas remains practically the same. Therefore the increase of pressure from P to P_2 takes place at **constant volume**.

When the gas acquires the temperature of the surroundings and a steady state has been reached the difference h_2 in the level of the liquid in the two limbs is again noted. The pressure P_2 of the enclosed gas is then given by

$$P_2 = P + \frac{h_2 \rho}{D}$$

Since the first process is adiabatic, then

$$P_1^{1-\gamma} T_1^\gamma = P^{1-\gamma} T^\gamma$$

$$\text{or} \quad \left(\frac{P_1}{P}\right)^{1-\gamma} = \left(\frac{T}{T_1}\right)^\gamma \quad \dots(i)$$

Where T_1 is the temperature of the surroundings and T is the temperature immediately after the adiabatic transformation when the pressure is atmospheric.

In the second case the temperature again rises from T to T_1 and the pressure rises from P to P_2 at constant volume.

$$\frac{P}{T} = \frac{P_2}{T_1}$$

$$\text{or} \quad \frac{P}{P_2} = \frac{T}{T_1} \quad \dots(ii)$$

From (i) and (ii), we have

$$\left(\frac{P_1}{P_2}\right)^{1-\gamma} = \left(\frac{P}{P_2}\right)^\gamma$$

$$\text{or} \quad \frac{P_1}{P} \cdot \frac{P^\gamma}{P_1^\gamma} = \frac{P^\gamma}{P_2^\gamma}$$

$$\text{or} \quad \frac{P_1}{P} = \left(\frac{P_1}{P_2}\right)^\gamma$$

Taking logarithms we have,

$$\log P_1 - \log P = \gamma (\log P_1 - \log P_2)$$

$$\therefore \gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2}$$

Aliter. Let P_1 and V_1 be the initial pressure and volume of the enclosed gas as shown at A in Fig. 7.5. If P is the atmospheric pressure which is the pressure of the gas after the adiabatic expansion and V_2 the corresponding volume which the gas should possess as shown at B , then the points A and B lie on the same adiabatic curve AB ,

$$\therefore P_1 V_1^\gamma = P V_2^\gamma$$

$$\text{or} \quad \left(\frac{V_2}{V_1}\right)^\gamma = \frac{P_1}{P} \quad \dots(i)$$

If P_2 is the pressure and V_2 the corresponding volume which the gas should possess after the room temperature has been attained as

shown at C , then the point A and C will be on the same isothermal curve AC as there is no temperature change from A to C .

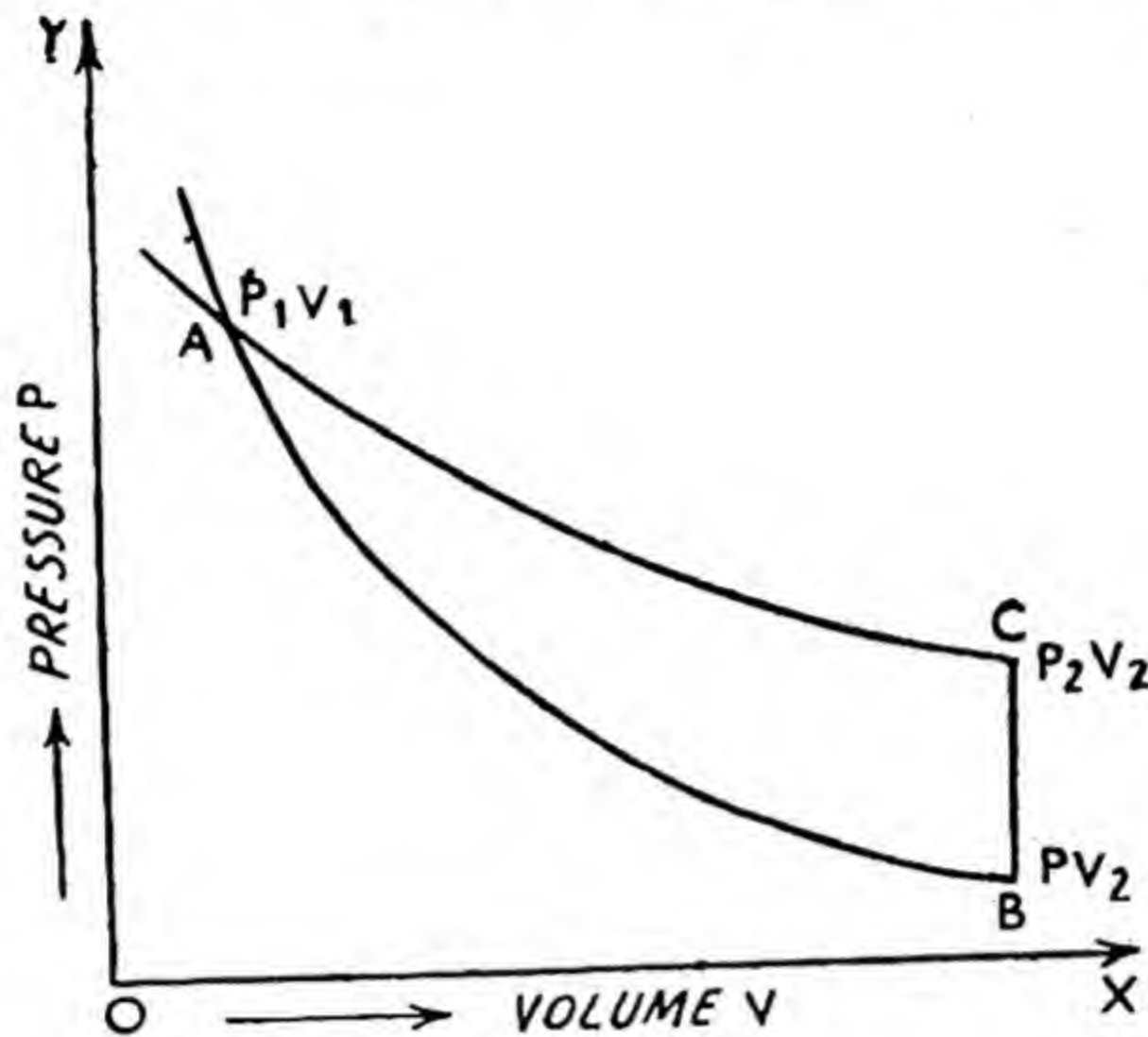


Fig. 7.5

$$\therefore \quad P_1 V_1 = P_2 V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \text{--- (ii)}$$

Substituting the value of $\frac{V_2}{V_1}$ in (i) we have

$$\left(\frac{P_1}{P_2}\right)^\gamma = \frac{P_1}{P}$$

$$\text{or } \gamma(\log P_1 - \log P_2) = \log P_1 - \log P$$

$$\therefore \gamma = \frac{\log P_1 - \log P}{\log P_1 - \log P_2} \quad \text{--- (iii)}$$

This relation is the same as desired above.

Thus γ can be calculated if P , P_1 and P_2 are known.

A very convenient approximation can be made if P_1 and P_2 are only slightly greater than P , an adjustment easily obtainable by arranging pressure P_1 in flask to be initially slightly greater than the atmospheric pressure.

Rearranging and substituting the values in relation (iii), we have

$$\gamma = \frac{\log \frac{P_1}{P}}{\log \frac{P_1}{P_2}} = \frac{\frac{\log \left(P + \frac{h_1 \rho}{D} \right)}{P}}{\frac{\log \left(P + \frac{h_2 \rho}{D} \right)}{P}} = \frac{\log \left(1 + \frac{h_1 \rho}{D} \times \frac{1}{P} \right)}{\log \left(1 + \frac{h_1 \rho}{D} - \frac{h_2 \rho}{D} \right)}$$

But $\log_e (1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 \dots$ from a well known formula in mathematics where $x < 1$.

$$\begin{aligned} \therefore \gamma &= \frac{\frac{h_1 \rho}{D} \times \frac{1}{P}}{\frac{h_1 \rho}{D} - \frac{h_2 \rho}{D}} \\ &= \frac{\frac{h_1}{P}}{P + \frac{h_2 \rho}{D}} \\ &= \frac{h_1/P}{(h_1 - h_2)/P} = \frac{h_1}{h_1 - h_2} \end{aligned}$$

If h_1, h_2 are small compared with P . Since $P + \frac{h_2 \rho}{D}$ is then equal to P , to very good approximation, we have finally

$$\gamma = \frac{h_1/P}{(h_1 - h_2)/P} = \frac{h_1}{h_1 - h_2}$$

This method gives fairly accurate value of γ and is very convenient to use in the laboratory.

Sources of error. When the stop cock is opened, more of the gas rushes out than is necessary to make the pressure atmospheric. The pressure of the gas inside therefore becomes less than the atmospheric and air from outside rushes in and so on. In this way oscillations are set up and it takes a considerable time for the pressure to become atmospheric. The stop cock S should be closed at the instant when during the oscillation, the pressure is just atmospheric, which is very difficult to judge.

Expected Questions

- I. (a) Explain and state the general gas equation.
(b) What is meant by (i) Isothermal change (ii) an adiabatic change. Illustrate them by examples. (A.M.I.E.)
2. Deduce the relation between the pressure, volume and temperature of a perfect gas undergoing an adiabatic change. (A.M.I.E.)
3. Describe expressions for the work done when a gas expands (i) isothermally (ii) adiabatically when the mass of the gas is (a) m gms (b) 1 gm-molecule. (A.M.I.E.)
4. Define the compressibility of a gas. Show that adiabatic compressibility is $\frac{1}{\gamma}$ times the isothermal compressibility.
5. Explain with a neat sketch the method of finding out the value of γ .

CHAPTER VIII

KINETIC THEORY OF GASES

8.1. Introduction. Danial Bernouli in 1730 suggested a kinetic theory of matter based on two assumptions.

(i) that matter is not continuous but consists of small aggregates, called molecules with inter spaces between them.

(ii) that the molecules are in a continuous state of agitation.

Both these assumptions are supported by experimental evidence. The kinetic theory of solids and liquids is not yet in a full state of development but the kinetic *theory of gases* can fully account for the various phenomenon in gases.

8.2. Kinetic Theory of Gases. The kinetic theory of gases has been highly succesful in explaining the behaviour of gases. The essential features are :—

(i) All gases are made of very tiny particles called molecules. The molecules of a gas are alike and differ from the molecules of other gases.

(ii) The size of the molecules is negligible i.e., the molecules are mere point masses as compared to the distance between them.

(iii) The molecules are continuously in motion. Their motion is absolutely haphazard and irregular. They have valocities in all directions ranging from zero to infinity. The gas is said to be in a state of molecular choas. The velocity of the molecules increases with temperature.

(iv) In a steady state the molecules are continously colliding against each other and with the walls of the containing vessel. Between two collisions a molecule moves in a straight line. The paths they follow while moving inside the gas are quite irregular and *zig-zag* as shown. The individual lengths of these paths vary winthin wide limits but the average value of a large number of such paths has a value at any temperature known as mean free path.

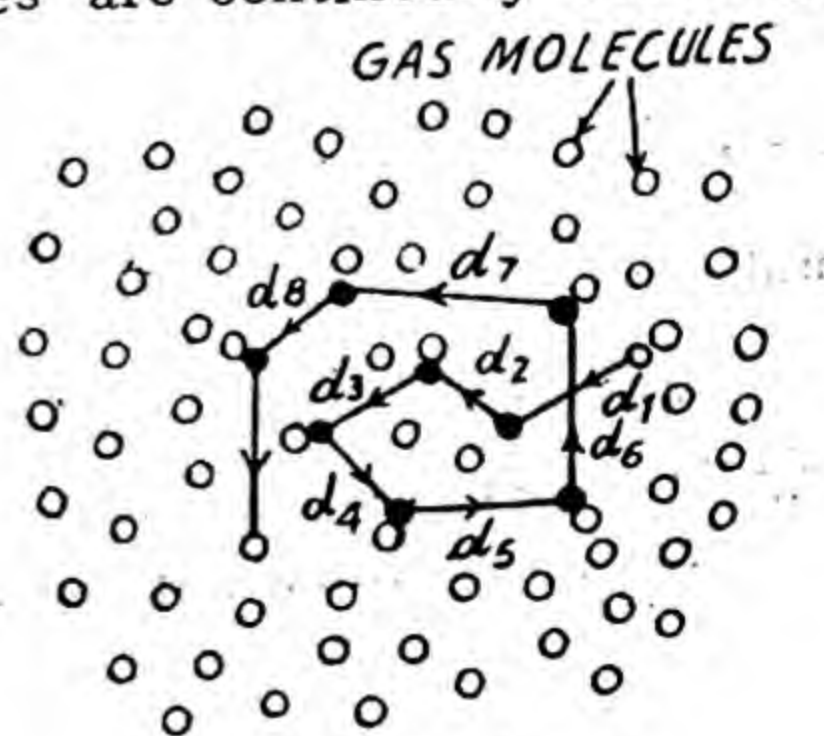


Fig. 8-1

\therefore Mean free path $(\lambda) = \frac{d_1 + d_2 + d_3 + \dots + d_n}{n}$ where d_1, d_2, d_3 etc. are the individual paths.

(v) The time during which a collision takes place is negligible as compared to the time required to traverse the free path i.e., the collisions are instantaneous.

(vi) The molecules in their motion collide with one another and with the walls of the containing vessel. At each collision their velocities are altered in direction and magnitude, yet in the steady state the collisions do not affect the molecular density of the gas i.e., the number of molecules per c.c. of the gas remains constant.

(vii) The molecules are perfect elastic spheres and exert negligible force of attraction or repulsion on another or on the walls of the containing vessel. In other words their encounters (collisions) with each other and with the walls of containing vessel are perfectly elastic and no energy is lost during encounter or collision.

We have seen that the molecules in a gas move randomly in all directions with all possible velocities. We normally consider three types of velocities as given below.

(i) **Mean velocity or average velocity.** If n molecules of a gas having velocities $v_1, v_2, v_3 \dots v_n$ are considered, then the mean or average velocity

$$C = \frac{v_1 + v_2 + v_3 + \dots + v_n}{n}$$

(ii) **Root mean square (R.M.S.) velocity.** Root mean square velocity of the n molecules is the square root of the mean of the squares of the individual velocities. Mathematically,

$$C_{r. m. s} = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

It is found that although due to the repeated collisions, the individual velocities may change, but the *r. m. s.* velocity remains constant so long as temperature remains constant.

The root mean square velocity can also be calculated from the relation.

$$C_{r. m. s} = \sqrt{\frac{3TK}{m}}$$

Where T = absolute temperature of the gas.

K = Boltzmann's constant and

m = mass per molecule of the gas.

$$\text{or } C_{r. m. s} \propto \sqrt{T}$$

(iii) **Most probable velocity.** If the molecules of a gas, possessing different individual velocities be grouped together, then it is seen that the number of particles possessing different velocities is different. If the distribution of the velocities of molecules is plotted as function of the number of molecules,

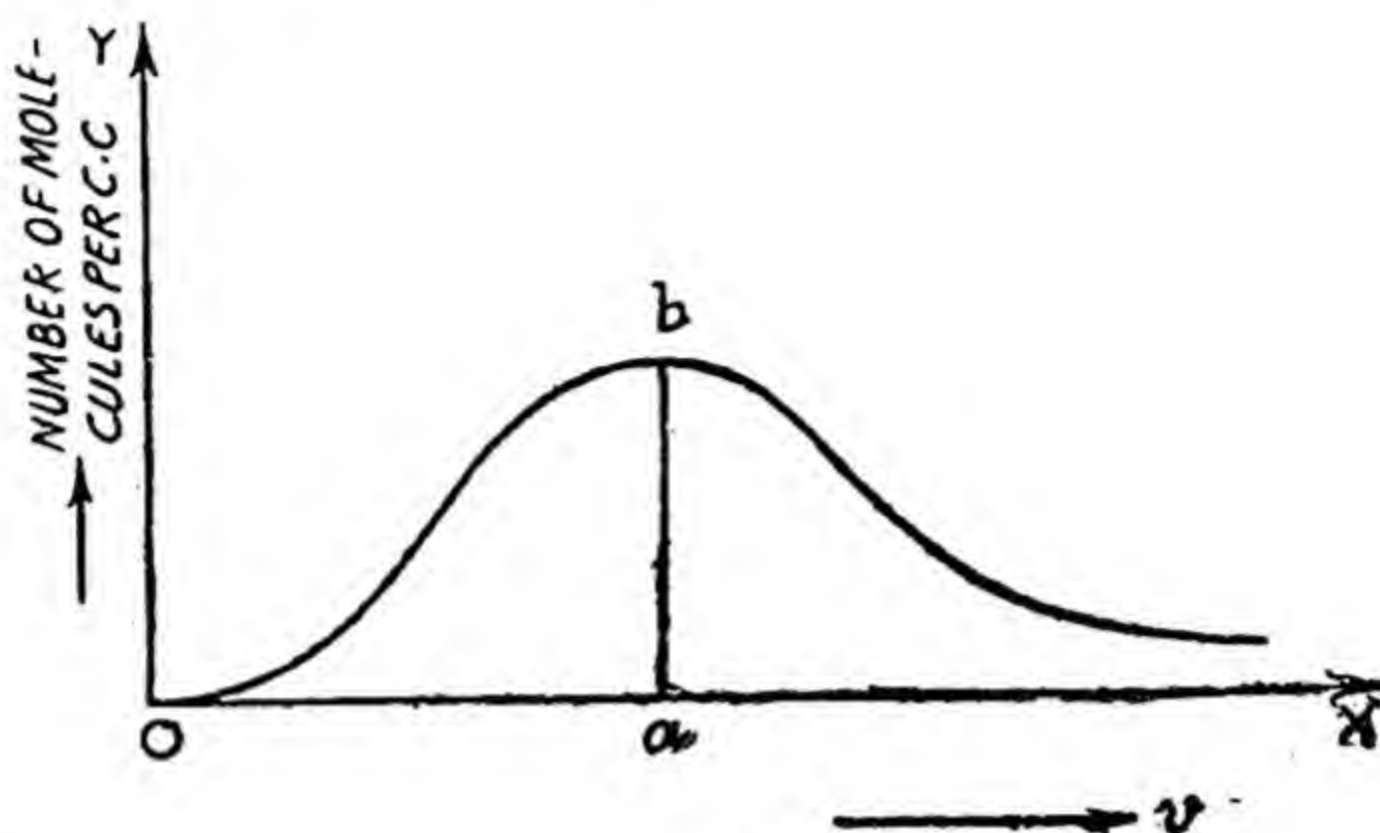


Fig. 8.2

we obtain a curve known as *Maxwell's distribution curve* as shown in Fig. 8.2. From the curve it is found that the greatest number of molecules at any temperature move with a velocity of Oa . This velocity is known as most probable velocity of the molecules and maximum number of molecules (as shown by ordinate ab) have the most probable velocity.

Most probable velocity is defined as that velocity with which the largest number of molecules in a gas are found to move at any given temperature.

The value of this velocity is given by the formula as

$$v_m = \sqrt{\frac{2kT}{m}}$$

here k , T and m have the usual meanings.

(iv) **Relation between mean velocity and root mean square velocity.** Clerk Maxwell has shown how the magnitudes of the molecular velocities are distributed in a gas in thermal equilibrium and from the theory the relation between c and C has been deduced out. They are related as follows.

$$c = \sqrt{\frac{8}{3\pi}} C$$

This numerical factor $\sqrt{\frac{8}{3\pi}}$ is very nearly equal to $\frac{12}{13}$ so that c is about $\frac{12}{13}$ of C , the mean velocity being some what smaller than the root mean square velocity.

8.3. Pressure of a gas. The molecules in their random motion will not only collide with one another, but also impinge on the walls of the containing vessel, thereby transmitting a definite momentum to the walls. Since the number of molecules making such impacts with the walls is very great, the walls will experience an almost continuous force per unit area known as pressure. Hence according to kinetic theory, the pressure exerted by a gas is merely the total momentum communicated to the walls of the containing vessel per second per unit area due to the impacts of the molecules of the gas. An expression for the pressure exerted by a gas can be found as follows.

Imagine a perfect gas contained in a cubical vessel of side l , with its edges parallel to the co-ordinate axes as shown in the Fig. 8.3. We assume that the collisions with the walls of the containing vessel are perfectly elastic. Let there be n molecules in the vessel, each of mass m .

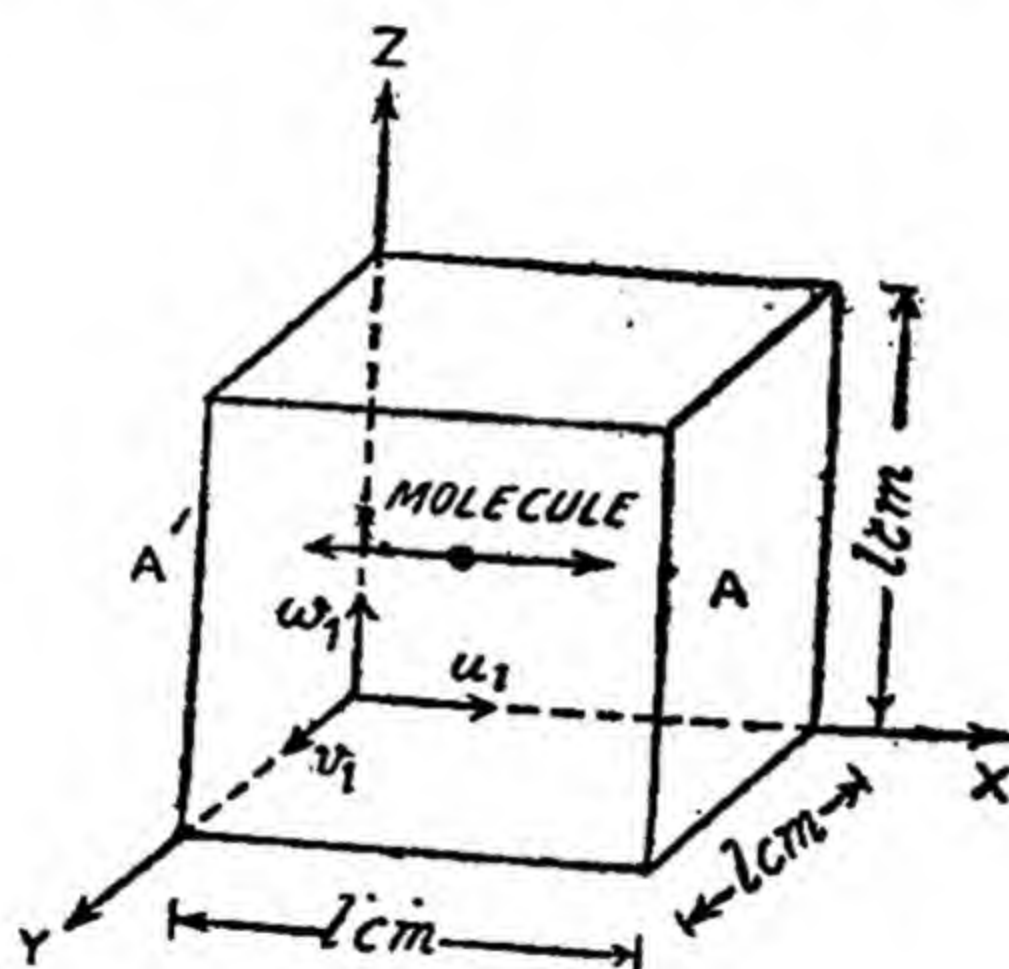


Fig. 8.3.

Let us now focus our attention on one molecule having velocity C_1 . This velocity can be resolved into three components u_1 , v_1 and w_1 along the X , Y and Z axes respectively as shown. The co-ordinate axes are supposed to be parallel to the sides of the cube. Then

$$C_1^2 = u_1^2 + v_1^2 + w_1^2$$

Consider the motion in a direction perpendicular to the face A . The molecule strikes the face A with a velocity u_1 and rebounds with the same velocity in the backward direction, since the collision is perfectly elastic. It means that if the velocity is u_1 before collision then it will $(-u_1)$ after collision. Similarly, its momentum is mu_1 before and $(-mu_1)$ after collision. Hence the change in momentum per collision per molecule is

$$mu_1 - (-mu_1) = 2mu_1$$

The molecule now travels from A to A' . It strikes A' and travels back again to A after covering a distance $2l$ (twice the length

of the sides of the cube). The time taken by the molecule to go to the other face and then to come back is $\frac{2l}{u_1}$.

$$\therefore \text{Nume of impacts per second} = \frac{u_1}{2l}$$

$$\begin{aligned} \text{The rate of change of momentum} &= 2mu_1 \cdot \frac{u_1}{2l} \\ &= \frac{mu_1^2}{l} \end{aligned}$$

Now according to Newton's second law, the rate of change of momentum is equal to the impressed force. If F_1 is the impressed force, then

$$F_1 = \frac{mu_1^2}{l}$$

Similarly the force F_2 due to the impact of another molecule having a velocity C_2 , whose three rectangular components are u_2, v_2 and w_2 , is given by

$$F_2 = \frac{mu_2^2}{l}$$

and o o n.

Hence the total force F_x on the face A due to impacts of all the n molecules is given by

$$\begin{aligned} F_x &= \frac{mu_1^2}{l} + \frac{mu_2^2}{l} + \dots + \frac{mu_n^2}{l} \\ &= \frac{m}{l} [u_1^2 + u_2^2 + \dots + u_n^2] \end{aligned}$$

Since pressure is the force per unit area, the pressure P_x on the face A is given by

$$\begin{aligned} P_x &= \frac{F_x}{\text{Area}} = \frac{m}{l \times (l \times l)} (u_1^2 + u_2^2 + \dots + u_n^2) \\ &= \frac{m}{V} [u_1^2 + u_2^2 + \dots + u_n^2] \end{aligned}$$

Similarly for the face B perpendicular to the Y axis the pressure.

$$P_y = \frac{m}{V} (v_1^2 + v_2^2 + \dots + v_n^2)$$

and for the face C perpendicular to the Z -axis, the pressure

$$P_z = \frac{m}{V} (w_1^2 + w_2^2 + \dots + w_n^2)$$

Since the pressure exerted by a gas is the same in all directions, the average pressure P of the gas is given by

$$P = \frac{P_x + P_y + P_z}{3}$$

$$\frac{m}{3V} \left[(u_1^2 + u_2^2 + \dots + u_n^2) + (v_1^2 + v_2^2 + \dots + v_n^2) + (w_1^2 + w_2^2 + \dots + w_n^2) \right]$$

Since $V = \text{volume} = \frac{1}{3} \frac{m}{V} [(u_1^2 + v_1^2 + w_1^2) + (u_2^2 + v_2^2 + w_2^2) + \dots + (u_n^2 + v_n^2 + w_n^2)]$

$$C^2 = u_1^2 + v_1^2 + w_1^2, \quad C^2 = u_2^2 + v_2^2 + w_2^2, \quad \dots \quad C^2 = u_n^2 + v_n^2 + w_n^2$$

$$\therefore P = \frac{1}{3} \frac{m}{V} (C_1^2 + C_2^2 + \dots + C_n^2) = \frac{1}{3} \frac{mnC^2}{V}$$

Where $C^2 = \frac{C_1^2 + C_2^2 + \dots + C_n^2}{n}$

and C is known as the root mean square velocity of the molecules.

If M be the total mass of the gas then,

$$M = mn$$

and

$$\frac{M}{V} = \rho$$

where ρ is the density, then

$$P = \frac{1}{3} \rho C^2$$

Relation between pressure and kinetic energy. The pressure exerted by the gas is given by the relation,

$$\begin{aligned} P &= \frac{1}{3} \rho C^2 \quad (\text{as proved above}) \\ &= \frac{2}{3} \times \frac{1}{2} \rho C^2 \\ &= \frac{2}{3} E \end{aligned}$$

where E is the mean kinetic energy per unit volume of the gas. Hence the pressure of the gas is equal to $\frac{2}{3}$ of the translational kinetic energy of the molecules in a unit volume.

Kinetic energy per gm.-molecule. From the relation,

$$P = \frac{1}{3} \frac{mnC^2}{V}$$

we have

$$PV = \frac{1}{3} mnC^2 \quad \dots (i)$$

Now according to the perfect gas equation

$$PV = RT$$

where

V = Volume per gm. molecule

R = Universal gas constant

If in relation (i) V is also the gram molecular volume, then

$$mn = M$$

will be the mass per gm-molecule. Hence the relation (i) becomes

$$\frac{1}{3} MC^2 = RT$$

or $\frac{1}{2} MC^2 = \frac{3}{2} RT$

Where $\frac{1}{2} (MC^2)$ is the kinetic energy per gm. molecule of any gas at the absolute temperature T .

Hence the kinetic energy per gm-molecule of any gas at the absolute temperature T is equal to $\frac{3}{2} RT$.

Root-mean square velocity. From the relation, $P = \frac{1}{3} \rho C^2$ it is clear that

$$C = \sqrt{\frac{3P}{\rho}} \quad \dots(i)$$

Hence this expression gives the root mean square velocity in terms of the pressure of a gas P and the density of the gas ρ .

Further we have $\rho = \frac{M}{V}$ where M is the molecular weight and V is the molar volume.

$$\therefore P = \frac{1}{3} \frac{M}{V} C^2$$

or $PV = \frac{1}{3} MC^2$

But $PV = RT$ (gas equation)

$$\therefore \frac{1}{3} MC^2 = RT$$

or $C = \sqrt{\frac{3RT}{M}} \quad \dots(ii)$

But $M = mN$

where $N = \text{Avogadro's number.}$

$$\therefore C = \sqrt{\frac{3RT}{mN}}$$

Now $\frac{R}{N} = k.$

$$\therefore C = \sqrt{\frac{3kT}{m}} \quad \dots(iii)$$

Since $\frac{R}{M} = r$ hence from equation (ii) we have

$$C = \sqrt{3rT} \quad \dots(iv)$$

Where r is the characteristic gas constant.

8.4. Kinetic interpretation of Temperature. We have derived the relation $P = \frac{1}{3} mnC^2$ for the pressure of a gas, where n is the number of

molecules in a unit volume of the gas. Multiplying by V , the volume of a gram molecule of the gas, we have,

$$PV = \frac{1}{3} mnV C^2 = \frac{1}{3} mNC^2$$

Where $nV = N$, the number of molecules in one gram molecule of the gas, or the Avogadro number as it is generally called.

Let

$$M = mN$$

∴

$$PV = \frac{1}{3} MC^2 \quad (i)$$

According to the perfect gas equation.

$$PV = RT \quad (ii)$$

Equating (i) and (ii) we have

$$C^2 = \frac{3R}{M} T$$

In other words, C^2 is proportional to the absolute temperature T .

At $T=0$,

$$C=0$$

Hence the absolute zero of temperature is that temperature at which the linear velocities of the molecules of a gas are reduced to zero.

Now

$$C^2 = \frac{3R}{M} T = \frac{3R}{mN} T.$$

or

$$mC^2 = \frac{3R}{M} T.$$

or

$$\frac{1}{2} mC^2 = \frac{3}{2} \frac{R}{N} T$$

Where R/N is a constant for a gas and is called Boltzmann's constant denoted by the letter k .

So that,

$$\frac{1}{2} mC^2 = \frac{3}{2} kT$$

Where $\frac{1}{2} mC^2$ is the mean kinetic energy of a molecule of the gas.

Thus mean kinetic energy of a molecule of the gas,

$$E = \frac{3}{2} kT.$$

and $K. E.$ of a gram molecule of the gas $= \frac{3}{2} k.N.T.$

$$= \frac{3}{2} \cdot \frac{R}{N} \cdot N.T.$$

$$= \frac{3}{2} RT$$

In other words, the mean $K. E.$ per molecule or $K. E.$ of the gram molecule in a given mass of a gas is proportional to the absolute temperature T .

*This fact is referred as **Kinetic interpretation of temperature.***

8.5. Deduction of simple gas Laws. The various gas laws may be deduced on the basis of the kinetic theory as follows :

(i) **Boyle's Law.** We know that the pressure of a gas is given by the relation, $P = \frac{1}{3}mnC^2$ where n is the number of molecules in a unit volume of the gas.

Multiplying both sides by V , the volume of the gas, we have

$$PV = \frac{1}{3}mnVC^2 = \frac{1}{3}mNC^2$$

Where $N = nV$, the total number of molecules in volume V of the gas.

$\therefore PV = \frac{1}{3}mnC^2 = \text{a constant, because } mnC^2 \text{ is constant}$

Hence $PV = \text{Constant.}$

The heat energy of a body is the energy of motion of its molecules. When the temperature of the gas is kept constant the heat energy of a given mass and hence total kinetic energy of its molecules is constant.

\therefore Total $K.E. = \frac{1}{3}mnC^2$ is constant at constant temperature.

It follows, therefore that at constant temperature, $PV = \text{Constant.}$
Boyle's Law is thus easily accounted for.

(ii) **Perfect gas equation.** We have the relation, $P = \frac{1}{3}mnC^2 = \frac{1}{3}\rho C^2$ where $mn = \text{density of the gas.}$

Multiplying by V , the volume of a gram molecule of the gas, we therefore have.

$$PV = \frac{1}{3}\rho VC^2 = \frac{1}{3}MC^2 = \frac{2}{3} \cdot \frac{1}{2}MC^2$$

Where $PV = M = \text{the mass of a gram molecule of the gas, and therefore } \frac{1}{2}MC^2 \text{ its kinetic energy.}$

Now, we know, that the absolute temperature of a gas is proportional to its kinetic energy so that,

$$PV \propto \frac{1}{2}MC^2 \propto T$$

or $PV = T \times \text{a constant}$ or $PV = RT$ the standard gas equation where R is the gas constant for given molecule of the gas.

(iii) **Charles' Law.** It has been proved above that $PV = RT$.

If the pressure is kept constant $\frac{V}{T}$ is constant i.e., $V \propto T$. In other

words, the volume of a gas is directly proportional to the absolute temperature, which is **Charles' law.**

(iv) **Avogadro's Hypothesis.** Suppose there are two gases and m_1, n_1 and C_1 represent the mass per molecule, number of molecules per c.c. and root mean square velocity respectively for one gas and m_2, n_2 and

C_2 the corresponding values for the other gas. If the two gases exert the same pressure P , then

$$P = \frac{1}{3} m_1 n_1 C_1^2 = \frac{1}{3} m_2 n_2 C_2^2 \dots \dots \dots (i)$$

If the two gases are also at the same temperature there will be no transfer of heat energy from one to the other when they are mixed up. This is possible only if the mean kinetic energy per molecule in the two gases is equal. In other words,

$$\left[\frac{1}{2} m_1 n_1 C_1^2 = \frac{1}{2} m_2 n_2 C_2^2 \right] \quad \frac{1}{2} m_1 C_1^2 = \frac{1}{2} m_2 C_2^2 \dots (ii)$$

From (i) and (ii) we have

$$n_1 = n_2$$

In other words, *equal volumes of two gases, under the same conditions of pressure and temperature, contain the same number of molecules.* and this is **Avogadro's Hypothesis**

For convenience, N ($n V$) is usually taken to be the number of molecules in a gram molecule of the gas and is called **Avogadro's Number**.

Example 1. Calculate the root mean square velocity of the molecules of Nitrogen at 0°C . The density of nitrogen at N.T.P. is 1.25 gm./litre . Density of mercury 13.59 gm/c.c. and $g = 981 \text{ cm/sec}^2$.
(A. M. I. E.)

Normal pressure $P = 76.00 \text{ cm of mercury column.}$
 $= 76 \times 13.59 \times 981 \text{ dynes/cm}^2$.

density $\rho = \frac{1.25}{1000} = 0.00125 \text{ gm/c. c.}$

$$\begin{aligned} \text{R. M. S. velocity, } C &= \sqrt{\frac{3P}{\rho}} \\ &= \sqrt{\frac{3 \times 76 \times 13.69 \times 981}{0.00125}} \\ &= 4.93 \times 10^4 \text{ cm/sec.} \end{aligned}$$

Example 2. If the Avogadro's number N is 6.02×10^{23} and Boltzmann's constant $k = 1.38 \times 10^{-6} \text{ ergs/degree}$, what is the average velocity of a molecule of oxygen at 27°C . Convert this into Km./hour .
(A. M. I. E.)

The root mean square velocity

$$C = \sqrt{\frac{3RT}{M}}$$

Now $R = Nk = 6.02 \times 10^{23} \times 1.38 \times 10^{-6} = 8.31 \times 10^7$ ergs/degree = 8.31 joules/degree

Where N = Avogadro's number

k = Boltzmann's constant.

M = Molecular weight of oxygen = $2 \times 16 = 32$

$T = 273 + 27 = 300^\circ K$.

$$\therefore C = \sqrt{\frac{3 \times 8.31 \times 10^7 \times 300}{32}} = 48,350 \text{ cm/sec.}$$

$$= 483.50 \text{ metres/sec.}$$

Converting it into km/hour, we get.

$$C = \frac{483.5 \times 3600}{1000} = 1750 \text{ km/hr.}$$

Example 3. Given that the gram-molecular weight of a gas occupies 22.4 litres at N.T.P., calculate the r.m.s. velocities of Hydrogen gas, (i) at $0^\circ C$ and (ii) at $50^\circ C$. Assume the usual values for any physical constant. Density of mercury = 13.6 gms/c.c. and $g = 981 \text{ cm./sec}^2$.
(A. M. I. E.)

(i) Molecular wt. of Hydrogen in gms
= 2.

Density of gas at $0^\circ C$, $= \frac{2}{22400} \text{ gm./c.c.}$

$$\therefore \text{R.M.S. velocity } C = \sqrt{\frac{3P}{\rho}}$$

where

$$P = 76 \times 13.6 \times 981 \text{ dynes/sq. cm.}$$

$$\therefore C = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{2}}$$

$$= 146400 \text{ cms./sec.}$$

(ii) Assuming that pressure remains constant,

R.M.S. Velocity $\propto \sqrt{T}$

$$\therefore \frac{\text{R.M.S. Vel. at } 50^\circ C}{\text{R.M.S. Vel. at } 0^\circ C} = \sqrt{\frac{T}{T_0}} = \sqrt{\frac{273+t}{273+0}}$$

$$\text{R.M.S. Vel. at } 50^\circ C = 146400 \times \left(\frac{323}{273}\right)^{\frac{1}{2}}$$

$$= 159200 \text{ cms./sec.}$$

$$= 1592.00 \text{ metres/sec.}$$

Example 4. 32 grams of oxygen at N.T.P. occupy 22.3 litres. Deduce the r.m.s. velocity of the molecules at 20°C. (A.M.I.E.)

$$\rho_0 = \frac{32}{22.3 \times 10^3} \text{ gm./c.c.}$$

$$P_0 = 76 \times 13.6 \times 981 \text{ dynes/sq. cm.}$$

$$C_0 = \sqrt{\frac{3P_0}{\rho_0}} = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22300}{32}}$$

$$= 45040 \text{ cm./sec.}$$

$$\text{Now } \frac{C_0^2}{C_{20}^2} = \frac{273}{273+t} = \frac{273}{273+20}$$

$$\text{or } C_{20}^2 = C_0^2 \times \frac{273+20}{273}$$

$$\text{or } C_{20} = C_0 \sqrt{\frac{293}{273}}$$

$$= 45040 \times \sqrt{\frac{293}{273}}$$

$$= 47680 \text{ cms./sec.}$$

Example 5. Find the temperature at which r.m.s. velocity of Hydrogen will be double of its value at N.T.P. when the pressure remains constant.

$$\frac{\text{R.M.S. Velocity at } t^\circ\text{C}}{\text{R.M.S. Velocity at } 0^\circ\text{C}} = \sqrt{\frac{T}{273}} = \sqrt{\frac{273+t}{273}}$$

$$\text{or } \frac{2}{1} = \sqrt{\frac{273+t}{273}}$$

$$\text{Squaring both sides } \frac{4}{1} = \frac{273+t}{273}$$

$$\text{or } t = 273 \times 4 - 273 = 819^\circ\text{C}$$

Example 6. Find the kinetic energy of the molecules of 1 gm. of Helium at 29°C if $R = 8.31 \times 10^7 \text{ ergs/}^\circ\text{K}$ and molecular wt. of helium is 4.

$$K.E. \text{ per molecule} = \frac{3}{2} kT.$$

where k is the Boltzmann's constant.

If N is the Avogador's number and molecular weight of helium is 4, then

$$\text{No. of molecules in one gm.} = \frac{N}{4}$$

$$\therefore K.E. \text{ per gm. of Helium} = \frac{N}{4} \times \frac{3}{2} kT$$

But $k = \frac{R}{N}$

$$\begin{aligned} \therefore K.E. \text{ per gm. of Helium} &= \frac{N}{4} \times \frac{3}{2} \times \frac{R}{N} T \\ &= \frac{3}{8} RT \\ &= \frac{3}{8} \times 8.31 \times 10^7 \times 300 \\ &= 9.1 \times 10^9 \text{ ergs} \\ &= 910 \text{ joules} \end{aligned}$$

Example 7. The mass of an oxygen molecule is 5.28×10^{-23} gm. and its mean velocity at N.T.P. is 42500 cm./sec. Calculate the mean kinetic energy of an oxygen molecule at 50°C .

We know $c = \sqrt{\frac{8}{3\pi}} C$

\therefore Squaring $c^2 = \frac{8}{3\pi} C^2$

or $C = \sqrt{\frac{3\pi}{8}} c$

Root mean square velocity of oxygen at 0°C .

$$\begin{aligned} C_0 &= \sqrt{\frac{3\pi}{8}} \times 42500 \\ &= 46100 \text{ cms./sec.} \end{aligned}$$

Also $C \propto \sqrt{T}$

or $\frac{C_{50}^2}{C_0^2} = \frac{273+t}{273} = \frac{273+50}{273}$

or $C_{50}^2 = \frac{323}{273} \times (46100)^2$
 $= 2.52 \times 10^9 \text{ cm./sec.}$

The mean kinetic energy at 50°C .

$$\begin{aligned} &= \frac{1}{2} m C_0^2 \\ &= \frac{1}{2} \times 5.28 \times 10^{-23} \times 2.52 \times 10^9 \\ &= 6.65 \times 10^{-14} \text{ ergs} \\ &= 6.65 \times 10^{-21} \text{ joules} \end{aligned}$$

Example 8. Given Avogadro's number N as 6.02×10^{23} and Boltzmann's constant $= 1.37 \times 10^{-6}$ ergs per $^\circ\text{C}$. Calculate (a) The kinetic energy of translation of an oxygen molecule at 27°C (b) The total kinetic energy of an oxygen molecule at 27°C . (c) The total kinetic energy in joules of a gram molecule of oxygen at 27°C .

Oxygen is a diatomic molecule having three degrees of freedom of the motion of translation and two degrees of freedom of the motion of rotation *i.e.*, in all **five** degrees of freedom.

∴ (a) *K.E.* of translation per molecule

$$\begin{aligned}
 &= \frac{3}{2} kT. \\
 &= \frac{3}{2} \times 1.37 \times 10^{-6} \times (273 + 27) \\
 &= 6.165 \times 10^{-14} \text{ ergs} \\
 &= 6.165 \times 10^{-21} \text{ joules}
 \end{aligned}$$

(b) Total kinetic energy per molecule

$$\begin{aligned}
 &= \frac{5}{2} kT. \\
 &= \frac{5}{2} \times 1.37 \times 10^{-6} (273 + 27) \\
 &= 10.275 \times 10^{-14} \text{ ergs} \\
 &= 10.275 \times 10^{-21} \text{ joules}
 \end{aligned}$$

(c) Total *K.E.* per gm. molecule

$$\begin{aligned}
 &= \frac{5}{2} kT \times N \\
 &= 10.275 \times 10^{-21} \times 6.02 \times 10^{23} \\
 &= 6185.55 \text{ joules}
 \end{aligned}$$

Example 9. Calculate the specific heats of Helium at constant pressure and constant volume, given that the density of Helium at N.T.P. is 0.18 gm./litre and $J = 4.2 \times 10^7$ ergs/cal.

As the density of the gas is 0.18 gm./litre

∴ Volume of the gas for 1 gm. = $\frac{1000}{0.18}$ c.c.

We know from the gas equation, $PV = RT$

or $R = \frac{PV}{T}$

$$= \frac{(76 \times 13.6 \times 981) \times \frac{1000}{0.18}}{273}$$

Now

$$C_p = \frac{5}{2} R \text{ if } R \text{ is in heat units.}$$

If R is not in heat units, then divide R by J .

$$\begin{aligned}\therefore C_p &= \frac{5}{2} R/J \\ &= \frac{5 \times 76 \times 13.6 \times 981 \times 1000}{2 \times 0.18 \times 273 \times 4.2 \times 10^7} \\ &= 1.23 \\ \text{and } C_v &= \frac{3}{5} \times 1.23 \\ &= 0.74\end{aligned}$$

8.6. Degrees of freedom. To completely describe the motion of a particle in one plane only two quantities must be known say its two rectangular co-ordinates. Similarly for a particle moving in space three independent co-ordinates must be known to describe its motion. A molecule in a rigid body can have three motions of vibration along any of the three co-ordinate axes in addition to its three motions of translation. Hence to completely describe the state of motion of a rigid body six co-ordinates are required. **The degrees of freedom** may, therefore be defined as the total number of co-ordinates required to specify completely the position and configuration of any dynamical system.

Take the case of a monoatomic gas molecule i.e., a molecule made up of single atom only. This molecule can rotate about its

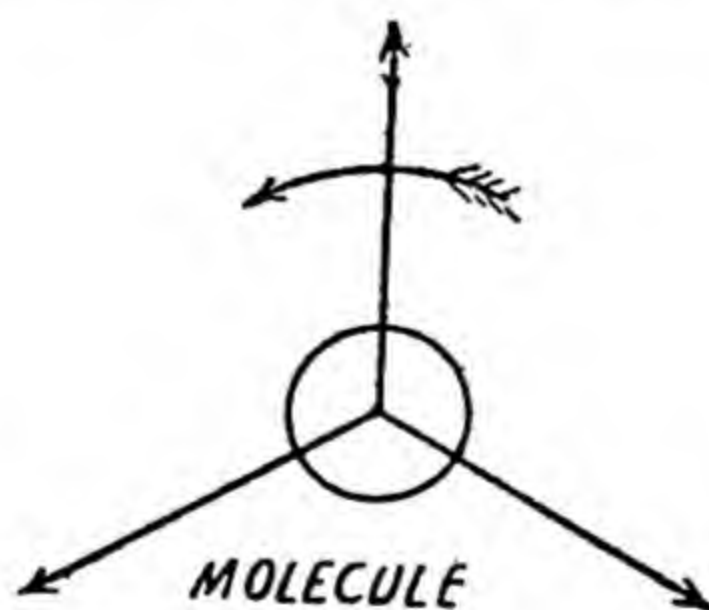


Fig. 8.4.

polar axis and can also move bodily in three mutually perpendicular planes X , Y and Z as shown in Fig. 8.4. Thus it has three translational degrees of freedom and one rotational, but the rotational degree of freedom has such a low moment of inertia that the effect of this is negligible. **Hence a molecule of monoatomic gas has 3 degrees of freedom of translation only.**

The molecule of a diatomic gas such as oxygen, hydrogen, nitrogen can be considered to have the shape of a dumb-bell, as shown in Fig. 8.5. Any such molecule has appreciable moment of inertia and it is capable of rotational as well as translational motions. Such a molecule can have a polar rotational motion as shown in the end

view and it may also have two perpendicular rotational movements as shown in the elevation and plan. But the moment of inertia of

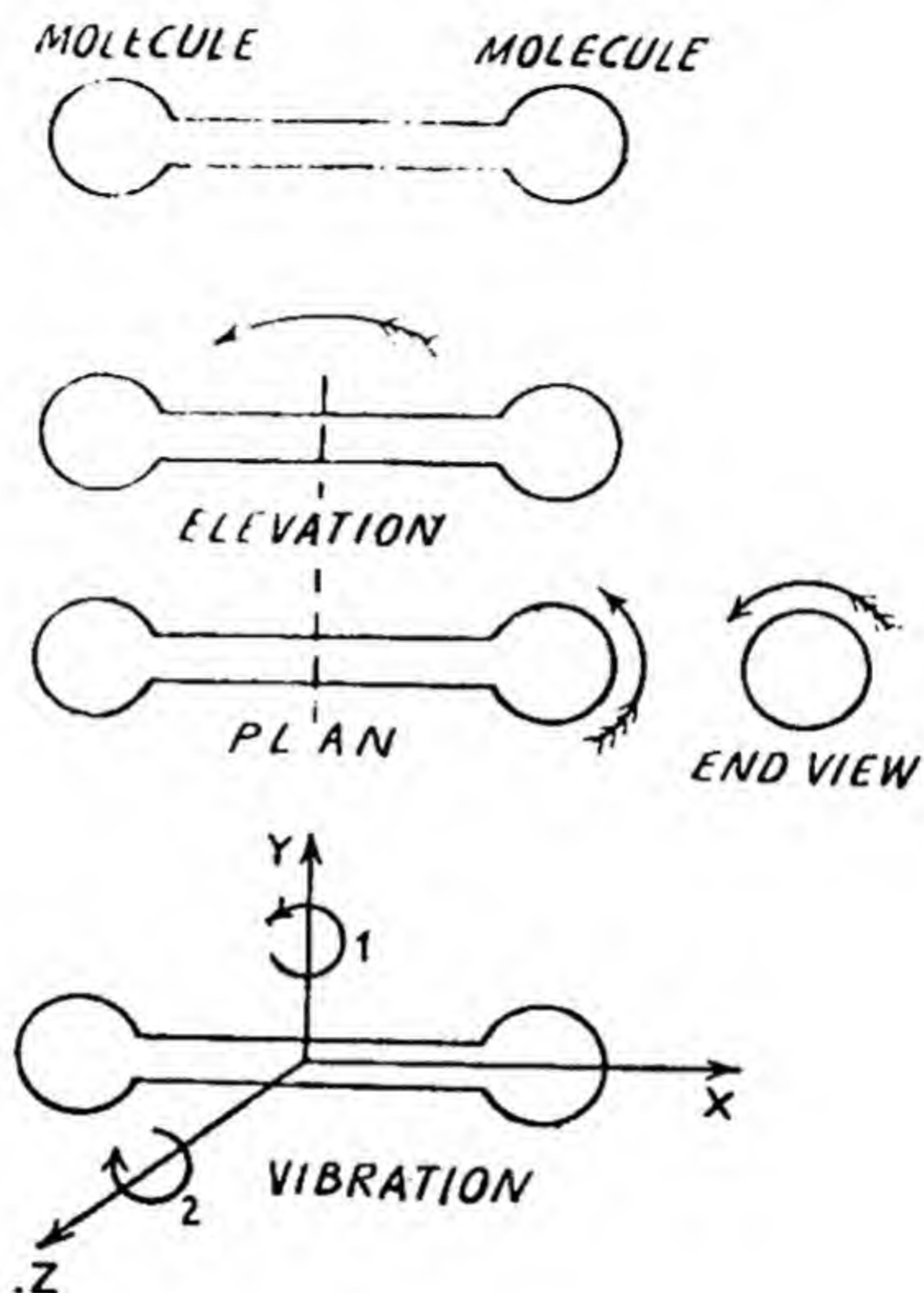


Fig. 8.5.

a dumb-bell molecule about its polar axis i.e., about the axis joining its molecules is much smaller than that about the axes perpendicular to this direction and hence the effect of this polar rotational motion is generally neglected. Thus we have three degrees of freedom of translational movement and two of rotational to give five in all. This is shown in Fig. 8.5, (vibration) in which the rotational moment have been resolved into two moments about two axes (1 and 2) perpendicular to the line joining the molecule.

The polyatomic molecules such as O_3 , CO_2 , H_2O consists of 3 or more atoms. If there are three atoms such as triatomic molecule that can be arranged as shown in Fig. 8.6 (a). Any such molecule has appreciable moment of inertia it is also capable of rotational as well as translational motion. Its rotational motion can be resolved into three motions about three mutually perpendicular axes x , y and z as shown in the Fig. 8.6 (b). Thus a polyatomic molecule possesses 6 degrees of freedom i.e., 3 translational and 3 rotational.

In general, the more complex the molecule, the greater will be the number of degrees of freedom possessed by it.

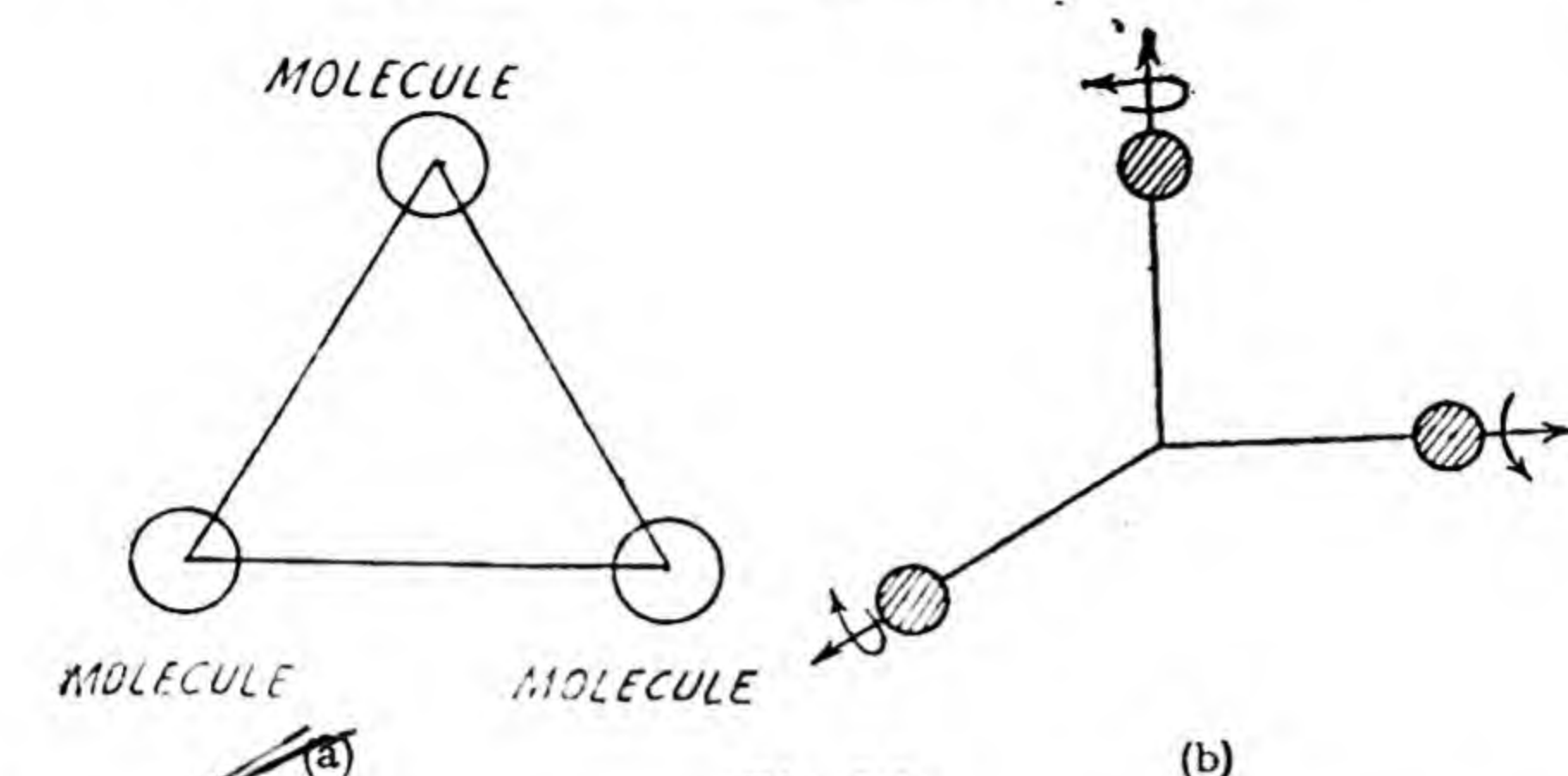


Fig. 8.6.

8.7. Law of equipartition of Energy. This law states, that "the total kinetic energy of a molecule in each degree of freedom is $\frac{1}{2} kT$." This law was first formulated by Maxwell in 1859 for translational degrees of freedom but later on Boltzmann extended it further to the rotational degrees of freedom etc.

In the treatment of kinetic theory of gases it is assumed that in the steady state

$$\overline{u^2} = \overline{v^2} = \overline{w^2}$$

\overline{u} , \overline{v} and \overline{w} are the average values of the component velocities.

$$\therefore \frac{1}{2} m \overline{u^2} = \frac{1}{2} m \overline{v^2} = \frac{1}{2} m \overline{w^2} = \frac{1}{3} \cdot \frac{1}{2} m C^2$$

$$\text{But } \frac{1}{2} m C^2 = \frac{3}{2} kT$$

$$\therefore \text{The K.E. per molecule per degree of freedom} = \frac{1}{3} \cdot \frac{3}{2} kT = \frac{1}{2} kT.$$

Thus we find that the total energy is divided equally among all the three degrees of freedom. The result is true for any number of degrees of freedom and is known as the law of equipartition of energy. It states that *for any dynamical system in thermal equilibrium the total energy is divided equally among all the degrees of freedom and the energy associated with one molecule per degree of freedom is equal to $\frac{1}{2} kT$.*

$$\text{The K.E. per gram molecule per degree of freedom} = \frac{1}{2} kT \times N = \frac{1}{2} RT$$

where N is the Avogadro's number and R the gas constant for a gram molecule.

8.8. Ratio of Specific Heats.

(i) **Monoatomic gas molecules.** A mono atomic gas molecule has only three degrees of freedom as it has only a motion of translation in space.

$$\therefore \text{Total K.E. per gm. molecule at } T^\circ K = 3 \times \frac{1}{2} RT = \frac{3}{2} RT.$$

and total $K.E.$ per gm. molecule at $(T+1)^\circ K = \frac{3}{2}R(T+1)$

But the increase in the total $K.E.$ per gm. molecule per degree rise of temperature is called the **molar specific heat** at constant volume i.e., C_v

$$\therefore C_v = R(T+1) - \frac{3}{2}RT = \frac{3}{2}R.$$

But $C_p - C_v = R$

$$\therefore C_p = C_v + R = \frac{3}{2}R + R = \frac{5}{2}R.$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.66$$

(ii) **Diatomic gas molecules.** As already explained the molecule of a diatomic gas has 5 degrees of freedom.

$$\therefore \text{Total } K.E. \text{ per gm. molecule at } T^\circ K = 5 \times \frac{1}{2}RT = \frac{5}{2}RT.$$

and total $K.E.$ per gm. molecule at $(T+1)^\circ K = \frac{5}{2}R(T+1)$

\therefore Increase in total energy per gm. molecule per degree rise of temperature, $C_v = \frac{5}{2}R(T+1) - \frac{5}{2}RT = \frac{5}{2}R.$

But $C_p = C_v + R = \frac{5}{2}R + R = \frac{7}{2}R.$

Hence $\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = \frac{7}{5} = 1.4$

(iii) **Triatomic gas molecules.** As already explained the molecule of a triatomic gas has 6 degrees of freedom.

$$\therefore \text{Total } K.E. \text{ per gm. molecule at } T^\circ K = 6 \times \frac{1}{2}RT = 3RT.$$

and total $K.E.$ per gm. molecule at $(T+1)^\circ K = 3R(T+1).$

$$\therefore C_v = \text{molar specific heat} = 3R(T+1) - 3RT = 3R.$$

$$\therefore C_p = 3R + R = 4R$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{4R}{3R} = 1.33$$

For more complex molecules γ approaches unity but is always greater than unity since $C_p > C_v$.

Kinetic energy and ratio of specific heats of gas molecules

Molecule	Degrees of freedom			Average K E	γ
	Translate	Rotation	Total		
Monoatomic	3	0	3	$\frac{3}{2}KT$	1.66
Diatomic	3	2	5	$\frac{5}{2}KT$	1.4
Polyatomic [tri-atomic]	3	3	6	$\frac{6}{2}KT$	1.33

8.9. Explanation of three states of matter on the basis of kinetic theory. Every substance whether solid, liquid or gaseous is made up of many millions of elementary particles known as molecules of the substance. **John Dalton** in 1803 was the first person to make use of this conception of matter. Later it was realised that molecules of a substance had some form of movement and there developed the **kinetic theory of Matter**, which in the hands of **Clark Maxwell** enabled the properties of a gas to be explained.

According to the kinetic theory, the molecules of a gas move about in all directions, making collisions for a short time with each other and with the walls of the containing vessel and rebounding from them. The motion of the molecules is a random or haphazard one and the average of the impacts per second of the molecules on one side of the container creates certain pressure there, which is the pressure of the gas.

Particles of matter have an attraction for each other which decreases as their distance apart increases.

1. SOLIDS. (i) *Shape and Volume.* The molecules of a solid are very closely packed. They attract each other with a very large force due to cohesion. They can not move about freely but can simply vibrate about their mean positions. This is why a solid has definite shape and volume.

(ii) *Elasticity and Rigidity.* If an external force is applied to change the size or shape of a solid it changes the distance between the molecules or their relative arrangement. On removing this force the molecules resume their original position and arrangement and the solid regains its original volume or shape. This explains the property of elasticity and rigidity of the solids.

(iii) *Expansion.* On heating the velocity of the molecules increases. They vibrate with greater and greater amplitude and the volume increases. The solids, therefore, expand on heating.

(iv) *Melting.* On further heating a stage reaches when the amplitude of vibrations becomes so large that a molecule can leave its mean position. The solid then changes into liquid form and the

temperature is known as *melting point*. The heat now supplied to the solid does not further increase the velocity of the molecules but is used in breaking the rigid structure of the molecules and takes them further away against their mutual attraction. This is then the latent heat of fusion.

2. Liquids. (i) *Shape and Volume.* The molecules of a liquid are farther apart than those of a solid. They attract each other with smaller force of cohesion. They can not leave the liquid but are free to move about anywhere in it. This is why a liquid has a definite volume but no shape of its own.

(ii) *Surface Tension.* A molecule lying within the liquid is attracted equally in all directions and hence the resultant force on it is zero. The molecules lying on the surface are attracted side ways and downward only. This explains why the free surface of a liquid behaves like a 'stretched membrane and gives rise to surface tension.

(iii) *Cooling due to Evaporation.* Different molecules have different velocities and the temperature of a liquid is determined by the mean square velocity. The molecules moving towards the surface are pulled downwards by the molecules lying below and so can not leave the liquid surface. But some of them which possess velocities much greater than, the average, manage to escape. This explains *Evaporation*.

As the molecules possessing large velocities escape, the mean square velocity of the molecules left behind decreases and, therefore, the temperature falls. This is why evaporation causes cooling.

(iv) *Diffusion.* The liquids slowly diffuse in to each other due to the motion of the molecules.

(v) *Expansion.* On heating the velocity of the liquid molecules also increases and they travel greater and greater distances. The liquid thus expands on heating.

(vi) *Boiling.* On further heating a stage reaches when the velocity of molecules becomes so large that they can overcome the force of attraction of other molecules and escape from the surface. The liquid begins to boil and the temperature is called the *boiling point*. The heat now supplied enables the molecules to overcome the force of attraction and the temperature does not rise further. This is called latent heat of vaporisation.

3. Gases. (i) *Shape and Volume.* The molecules of a gas are very much farther apart than those of a solid or a liquid. This can be seen from the fact that 1 c.c. of water changes into 1700 c.c. of steam. The force of attraction between the molecules of a gas is almost negligible and the molecule is free to wander over the entire space available to it. This is why a gas has neither a volume nor a shape of its own.

(ii) *Boyle's law.* When the gas is contained in a vessel, its molecules continuously strike against the walls and are turned back with equal and opposite velocities. The rate of change of momentum per unit area gives the pressure exerted by gas. When the volume of the vessel is increased, the number of molecules striking a unit area of walls in one second decreases. Hence the pressure is inversely proportional to volume. This explains Boyle's law.

(iii) *Regnault's Law.* When the vessel is heated the temperature of the gas and therefore, the velocity of the molecules increases. This brings about an increase in the rate of change of momentum per unit area per second. The pressure of a gas, therefore, is proportional to the absolute temperature.

8.10. Mean free path. According to kinetic theory of gases it is assumed that the molecules of a gas are in a state of continuous motion and their motion is absolutely haphazard and irregular. During their movement they go on colliding against each other. Between two collisions the molecules travel a certain distance in a straight line. This distance is called the free path. The particular direction of motion and velocity is changed only during collisions with other molecules or with the walls of the containing vessel. The molecule travels undisturbed in a straight line till it approaches very close another molecule when it is suddenly deflected due to the influence of the latter such a meeting of molecules is known as **encounter** and is of very short duration and is usually accompanied by changes in the velocities of the molecules. Hence the path of a single molecule will consist of a series of short zig zag paths as shown in Fig. 8.7. Some of these paths will be long, others will be short but the average of a large

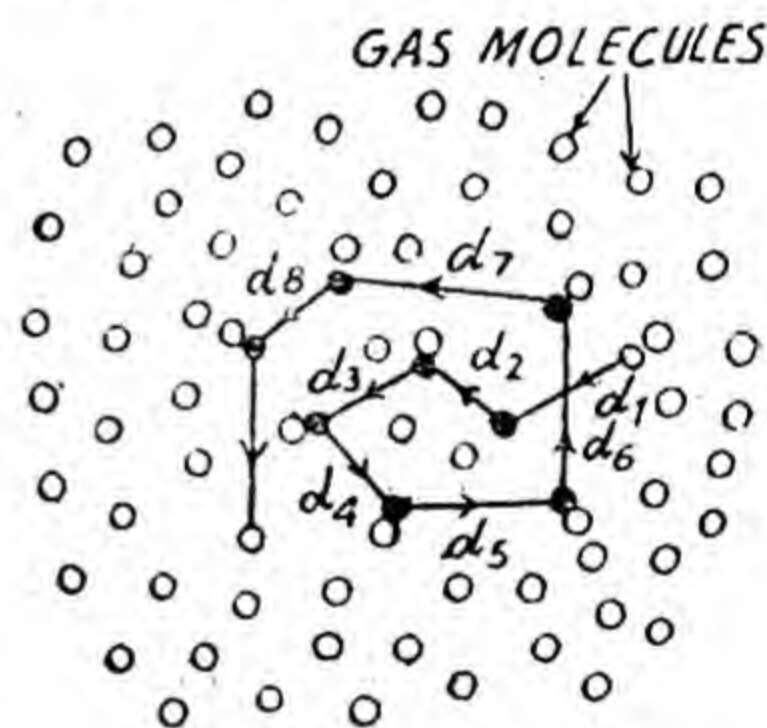


Fig. 8.7

number of such paths has a definite value at any temperature and is known as **mean free path** (λ).

If d_1, d_2, d_3 , etc. are the individual paths then the, mean free path is given by,

$$\lambda = \frac{d_1 + d_2 + d_3 + \dots + d_n}{N} = \frac{D}{N}.$$

Where D is the total path travelled in N collisions and is given by

$$D = d_1 + d_2 + d_3 + \dots + d_n$$

Hence the mean free path λ is defined as the *average distance travelled by a molecule between two successive collisions.*

$$\therefore \lambda = \frac{D}{N}.$$

8.11. Calculation of the mean free path. To simplify the calculations we suppose that,

(1) Only the molecule under consideration is in motion and all other molecules are at rest.

(2) The molecule has a sphere of influence around it. The radius of this sphere of influence is equal to the diameter d of the molecule as shown in the Fig. 8.8 (a)

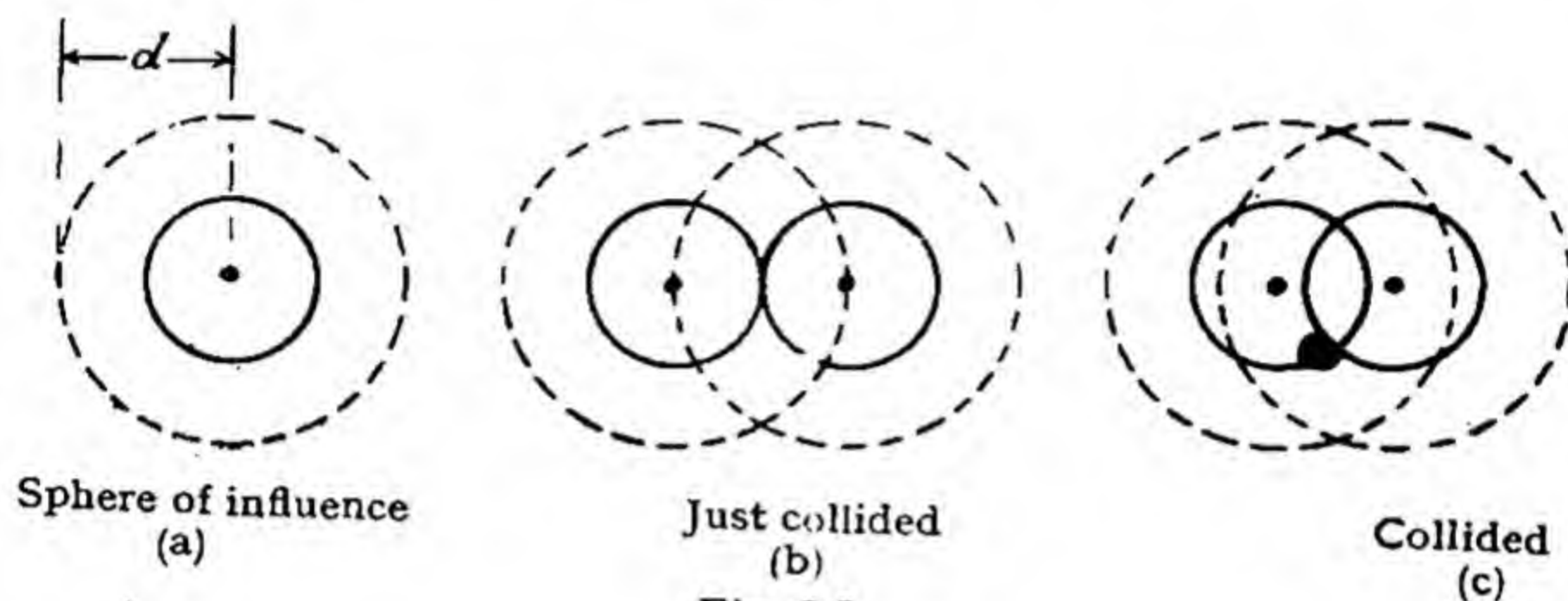


Fig. 8.8.

Theories

In other words it means the molecule can collide only with those molecules the centres of which lie at a distance d or less. A collision is shown in the Fig. 8.8 (b) and (c).

Consider now some particular molecule. Let it move about within the gas with a velocity C whereas all other molecules are at rest. As it moves its sphere of influence sweeps out in one second a cylinder whose cross-sectional area is πd^2 and whose length is the distance traversed in one second i.e., C . In one second the molecule under consideration collides with all the molecules the centres of which lie within a cylinder of radius d and length C .

\therefore the volume of the cylinder $= \pi d^2 C$.

Let the number of molecules per c. c. be n , then

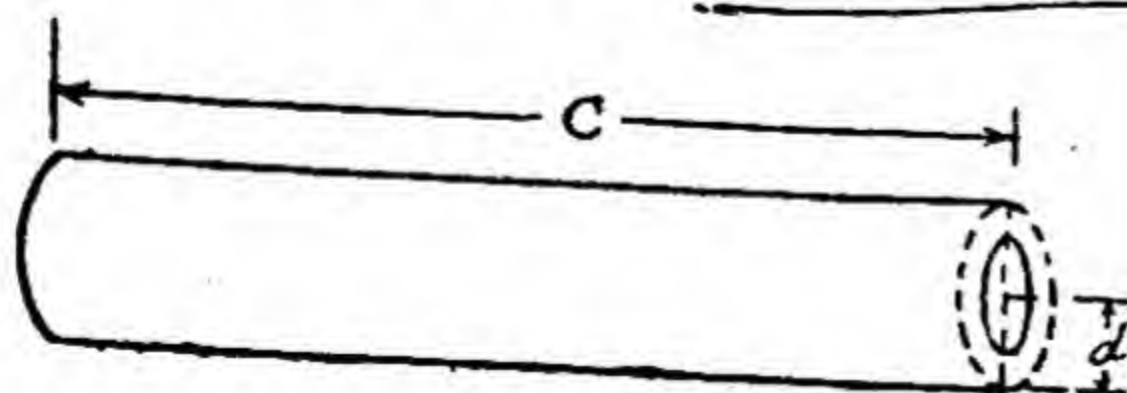


Fig. 8.9

Number of molecules in the cylinder $= \pi d^2 C n =$ the number of collisions per sec.

\therefore Average time between two successive collisions $= \frac{1}{\pi d^2 C n}$ sec.

Hence average distance between two successive collisions

$$= \frac{1}{\pi d^2 C n} \times C = \frac{1}{\pi d^2 n}$$

\therefore Mean free path, $\lambda = \frac{1}{\pi d^2 n}$

If m is the mass of one molecule, then

$mn = \rho$, the density of the gas. ✓

$$\therefore \lambda = \frac{m}{\pi d^2 mn} = \frac{m}{\pi d^2 \rho}$$

Hence the mean free path λ is inversely proportional to the density of the gas ρ which itself varies directly as the pressure and inversely as the absolute temperature. Therefore the mean free path is inversely proportional to pressure and directly proportional to the absolute temperature.

Example 10. The mean free path of the molecules of a gas is 2×10^{-5} cm. when there are 1.25×10^{19} molecules per cm^3 . Compute the diameter of the molecules.

Here $n = 1.25 \times 10^{19}$
 $\lambda = 2 \times 10^{-5}$ cms.

Diameter $d = ?$

Using the formula,

$$d^2 = \frac{1}{\pi n \lambda}$$

or $d = \frac{1}{\sqrt{\pi n \lambda}}$

All the letters are having the usual meanings and putting the given values we find,

$$\begin{aligned} d &= \frac{1}{\sqrt{\pi \times 1.25 \times 10^{19} \times 2 \times 10^{-5}}} \\ &= \frac{1}{\sqrt{\pi \times 2.5 \times 10^{14}}} = \frac{10^{-6}}{28.03} \\ &= 3.5 \times 10^{-8} \text{ cm.} \end{aligned}$$

8.12. Viscosity of a Gas on Kinetic Theory. Consider that a gas flows over a horizontal surface OX with a velocity small

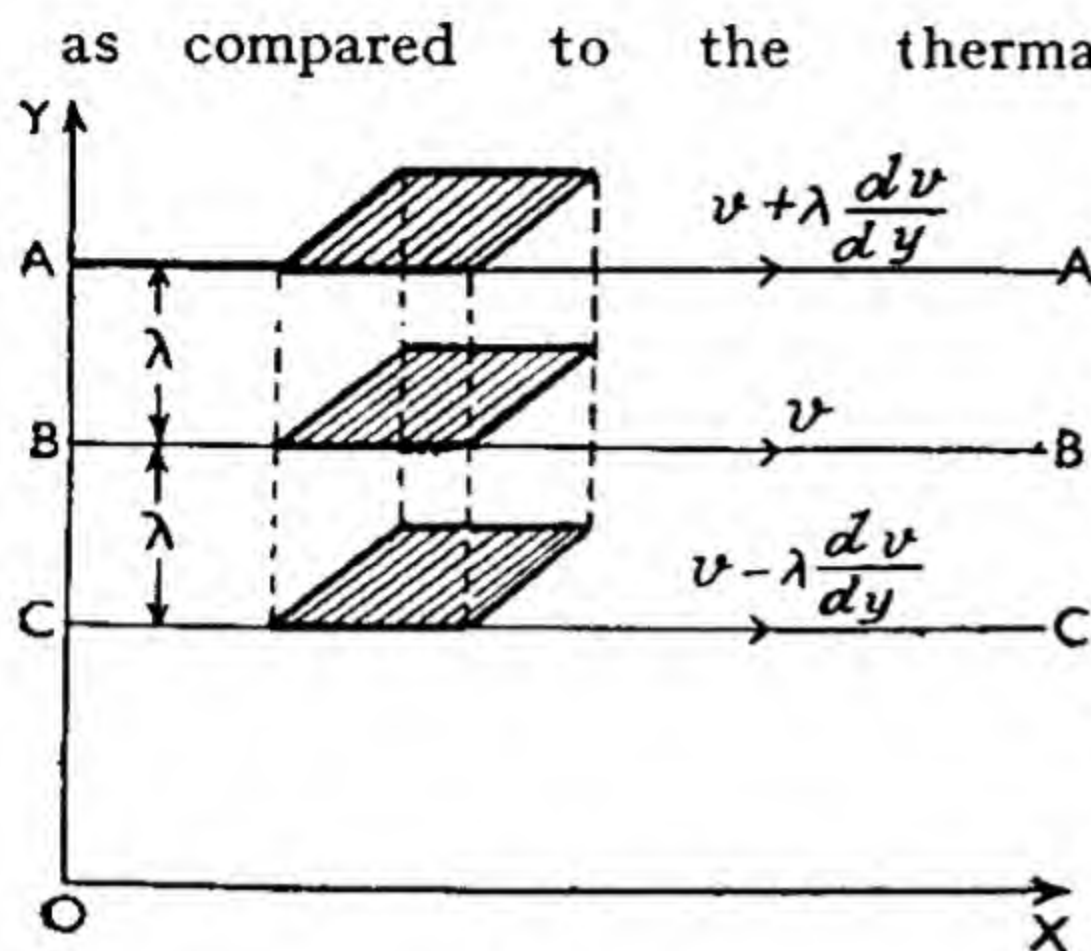


Fig. 8.10

as compared to the thermal velocity of the molecules in the direction OX . Then, the velocity of the layer in contact with the surface is zero and it increases as we go along OY in a direction perpendicular to OX at a uniform rate $\frac{dv}{dy}$.

Consider a layer BB at a certain distance from the fixed surface OX . The velocity with which the gas flows in this layer is v . Consider two layers AA and CC above and below BB respectively at a distance λ equal to the mean free path of the molecules so that the molecules moving vertically up or down do not have any collisions while moving between the two layers.

The velocity of gas in the layer $AA = v + \lambda \frac{dv}{dy}$

and the velocity of gas in the layer $CC = v - \lambda \frac{dv}{dy}$

Now, due to thermal velocities the molecules are moving in all directions. We can imagine them to be divided into 3 parts moving in *either direction* parallel to the X , Y and Z axes respectively, so that on an average one-sixth of the molecules move parallel to any *one axis* in *one* particular direction. There is thus a continuous interchange of molecules between the layers AA and CC . If n is the number of molecules per c. c., m the mass of each and c the velocity, then the number of molecules passing downwards from AA to CC per unit area of the layer BB in one second $= \frac{nc}{6}$

\therefore Forward momentum lost per unit area per second by the layer

$$AA = m \cdot \frac{nc}{6} \left(v + \lambda \frac{dv}{dy} \right)$$

Similarly the number of molecules moving upwards per unit area of the layer BB in one second $= \frac{nc}{6}$

\therefore Forward momentum gained per unit area per second by the

$$\text{layer } AA = m \cdot \frac{nc}{6} \left(v - \lambda \frac{dv}{dy} \right)$$

\therefore Net momentum lost by the layer AA per unit area per sec.

$$= \frac{mnc}{6} \left\{ \left(v + \lambda \frac{dv}{dy} \right) - \left(v - \lambda \frac{dv}{dy} \right) \right\}$$

$$= \frac{1}{3} mnc\lambda \frac{dv}{dy}$$

The layer CC below BB gains the same amount of momentum.

Hence the layer AA above BB tends to accelerate its motion and the layer CC below BB tends to retard its motion.

The backward dragging force per unit area = gain or loss of momentum per unit area in one second.

$$\therefore F = \frac{1}{3} mnc\lambda \frac{dv}{dy}$$

This must be equal to the tangential force $\eta \frac{dv}{dy}$ acting per unit area of the layer BB due to viscosity, η being the co-efficient of viscosity of the gas.

$$\therefore \eta \frac{dv}{dy} = \frac{1}{3} mnc\lambda \frac{dv}{dy}$$

$$\text{or } \eta = \frac{1}{3} mnc\lambda \quad [\because mn = \rho]$$

$$= \frac{1}{3} \rho c\lambda$$

The density of a gas increases with pressure but λ decreases in the same ratio so that $\rho\lambda$ remains constant.

Hence η is independent of pressure.

The density of a gas decreases with temperature where as λ increases in the same ratio. But the molecular velocity c is proportional to \sqrt{T} where T is the absolute temperature.

$$\therefore \eta \propto \sqrt{T}$$

$$\therefore \frac{\eta}{\eta_0} = \sqrt{\frac{T}{T_0}}$$

Expected Questions

1. (a) State the assumptions of Kinetic theory of gases and show that they lead to gas laws of a perfect gas. (A.M.I.E.)

(b) Distinguish between the following

(i) Mean or average velocity (ii) root mean square velocity (iii) most probable velocity of an assemblage of molecules. (A.M.I.E.)

2. (a) Derive an expression for the pressure of a gas on the basis of kinetic theory. (A.M.I.E.)

(b) Prove that the pressure of a gas is equal to $\frac{2}{3}$ of the translational kinetic energy of the molecules in a unit volume. (A.M.I.E.)

3. (a) Outline the essential features of kinetic theory of gases and apply it to account for the simple gas laws. (A.M.I.E.)

(b) What is the interpretation of temperature on this theory?

4. Deduce the values of two specific heats and of their ratio γ for (a) monoatomic gases (b) diatomic gases (c) Poly-atomic gases on the basis of the principle of equipartition of energy. (A.M.I.E.)

5. What is the meaning of mean free path of the molecules of a gas?

Show that it is equal to $\frac{1}{\pi n d^2}$ where n is the number of molecules per c.c. and d is the diameter of each molecule. Show that the mean free path is proportional to pressure. (A.M.I.E.)

6. Derive an expression for the viscosity of a gas on the basis of kinetic theory. (A.M.I.E.)

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CHAPTER IX

CHANGE OF STATE

9.1. When a substance like ice or paraffin wax is heated in a vessel, a temperature is reached when the substance begins to pass to the liquid state. This process of conversion of a solid into its liquid state on heating is known as **fusion** or **melting** and the temperature at which the substance begins to melt is known as the **melting point**. If a liquid is cooled, the reverse change takes place and the liquid is said to have solidified. The change of state from liquid to solid is called solidification or **FREEZING**. The temperature at which freezing takes place is called **freezing point**. If the pressure is unchanged a crystalline substance always melts or solidifies at the same temperature. In the case of some non-crystalline substances the melting and freezing points are not equal *i.e.*, butter melts at 32°C and freezes at about 23°C .

If the liquid is further heated, it is converted into vapour at a certain temperature. This process of conversion of a substance from its liquid to the gaseous or vapour state is called **vaporisation** and the temperature at which this change takes place is called the **boiling point** of the liquid. This is also a characteristic property of the substance but varies greatly with pressure.

The reverse process of the change of a vapour into its liquid state is known as **condensation**. Certain solids when heated are converted directly into vapour or gaseous state. This change of state is known as **sublimation**. The examples of such substances are *Camphor*, *ammonium chloride*, *iodine* etc.

9.2. Latent Heat. When a solid substance is heated, a thermometer placed in the solid shows that the heat absorbed by the solid goes on increasing the temperature until melting or fusion begins. On further heating more and more of the solid melts but *the temperature remains constant till the whole of the substance has melted*. Similarly if a liquid is continuously heated, its temperature gradually rises, till at a certain temperature the liquid begins to boil and changes into a vapour state. On further heating more and more of the

liquid is vaporised but the temperature remains constant till the whole of the liquid has vaporised.

The above two examples show that at the melting point and at the boiling point heat is continuously being supplied but the temperature remains constant. *This amount of heat which is absorbed during a change of state without causing a rise of temperature is called the latent heat.* (Latent means hidden)

There are two kinds of latent heat.

- (i) Latent heat of fusion.
- (ii) Latent heat of vaporisation.

Latent heat of fusion. *It is the quantity of heat required to change a unit mass of a solid at its melting point into the liquid state without change of temperature.*

Latent heat of Vaporisation. *It is the quantity of heat required to change a unit mass of a liquid at its boiling point from the liquid to the vapour state without change of temperature.*

Latent heat of fusion of ice is also known as the **Latent heat of water.** *It is defined as the amount of heat required to melt 1 gram of ice at 0°C into water at 0°C without change of temperature.* Latent heat of fusion of ice is 80 calories per gm. or 80 k. cal./kg. and latent heat of steam is 540 cal./gm. or 540 k. cal./kgm.

The latent heat of steam depends upon the temperature at which conversion from water to vapour state takes place and is given by the equation.

$$L = 538.86 + 0.5994 (100 - t^{\circ}\text{C}).$$

9.3. Laws of Fusion. The process of conversion of a solid into the liquid state is governed by the following laws known as the **laws of fusion.**

(i) Every substance when heated begins to melt or fuse at a particular temperature (melting point) which depends upon the pressure.

(ii) From the moment melting begins the temperature of the substance remains constant until the whole of the substance has melted.

(iii) Unit mass (1 gm or 1 kg) of every substance requires a definite amount of heat to change it from the solid to the liquid state without change of temperature. This heat is called the latent heat of fusion of the substance.

(iv) Every substance undergoes a change in volume on melting. Some substances like ice contract whereas others like paraffin wax expand on melting.

(v) The melting point of a substance which increases in volume on melting is raised with rise of pressure and of a substance which decreases in volume on melting, is lowered with rise of pressure.

9.4 Determination of Melting point of a Solid. *The melting point of a solid is the temperature at which it changes into the liquid state without change of temperature. The melting points of pure crystalline substances like naphthalene are always sharply defined. But amorphous or non crystalline substances like wax, rubber and glass pass more or less through a plastic stage and hence do not possess sharp melting points. The melting points of solids like wax or naphthalene which have low melting points can be found out by the following methods.*

1. **Capillary tube or Opacity method.** Take the substance in a

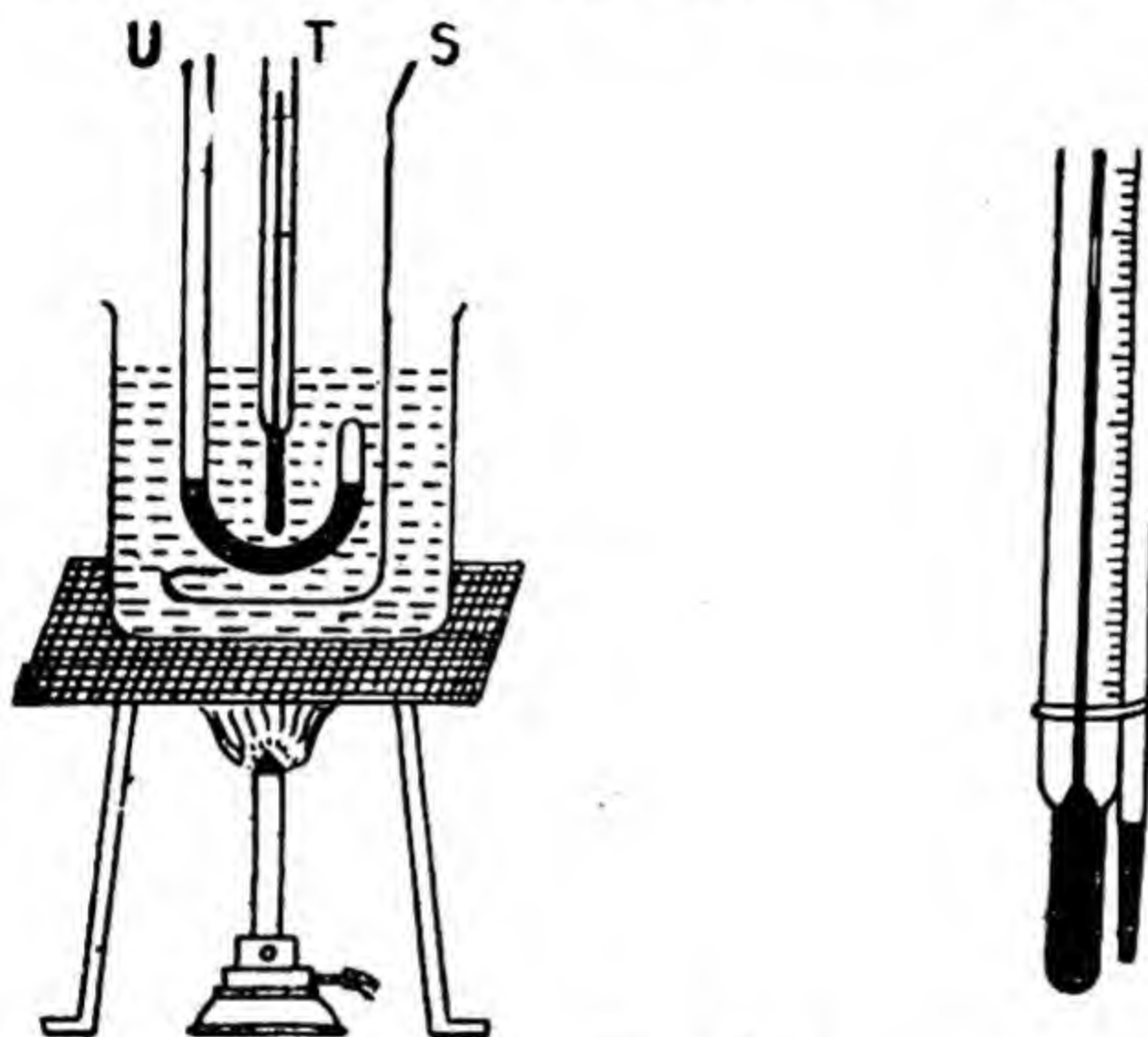


Fig. 9.1.

small dish and melt it. Insert one end of a small *capillary* tube into the dish. Some liquid will rise inside the tube due to capillary action. Seal the lower end of the tube in a flame and tie it to the stem of the thermometer near the bulb, by means of a thin rubber band as shown in Fig. 9.1. Suspend the thermometer along with the capillary tube in a beaker, about $\frac{3}{4}$ th filled with liquid in such a way that the open end of the capillary tube is above the liquid as shown in the figure.

[**Note.** (i) *The liquid in the beaker should be such that its boiling point is higher than the melting point of the substance under examination.*

(ii) *Water may be used to determine the melting point of paraffin wax and some oil or sulphuric acid to determine the melting point of sulphur.]*

Heat the liquid in a beaker from below and go on stirring it. Note the temperature at which the solid in the capillary tube just becomes clear and transparent due to melting. Remove the flame and allow the liquid to cool, stirring it all the time. Again note the temperature at which the melted solid just begins to

solidify i.e., it becomes opaque. The mean of these two temperatures is taken as the correct melting point of the substance.

2. Cooling curve method. The fact that during the process of conversion of a solid into a liquid state and vice versa, the temperature remains constant, is used to find the melting point of a substance. Take some substance such as paraffin wax or naphthalene in a small vessel say calorimeter or a beaker and heat to a temperature till the whole of it melts. Place a thermometer and a stirrer in it and remove the burner. Allow the liquid to cool and go on recording its temperature say after every minute. When the liquid starts solidifying, stop stirring but go on noting the temperature till the substance has cooled much below the solidifying point. The graph between time and temperature is plotted, the shape of the cooling curve thus obtained is shown in Fig. 9.2.

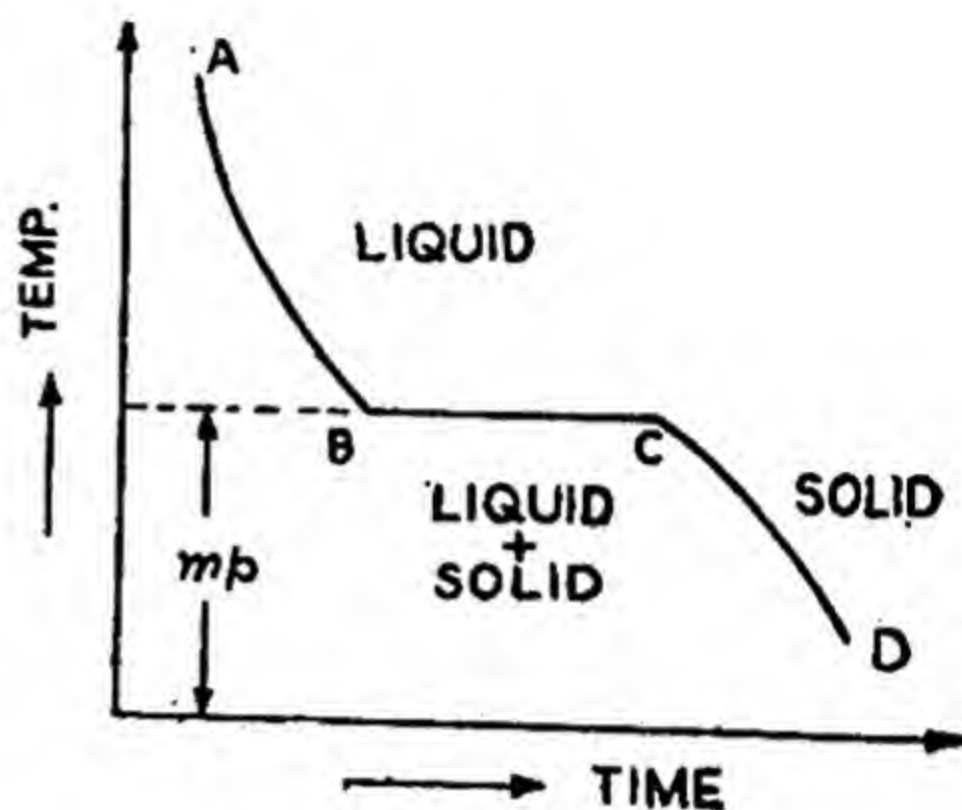


Fig. 9.2.

The part *AB* of the curve shows the liquid state of the substance as it is being cooled. The temperature goes on falling till the point *B* is reached where the solidification sets in. Now the temperature remains constant till the whole of the liquid has solidified as shown by the part *BC* of the curve which runs parallel to the time axis. During the part *BC* the substance is solidifying. Here the solid and liquid states exist together until the solidification started at point *B* ends at point *C*, the temperature remaining constant throughout. The part *CD* shows the solid state with a fall in temperature as the solid is being cooled. The temperature corresponding to the part *BC* of the curve is the **melting point** of the substance. This method is generally used for finding the melting points of metals, alloys and crystalline solids, as a curve with a definite stage of constant temperature is obtained with these.

9.5. Super cooling or super fusion. Most of the liquids if cooled in a pure state in a perfectly clean vessel, with least disturbance can be lowered to a temperature much below the normal freezing point without solidifying. For instance, if distilled water is taken in a glass test tube and cooled slowly without stirring it, then it can be cooled upto -10°C without any ice being formed. Water has been cooled to as low as -20°C by surrounding it with a liquid of the same density but lower freezing

point. Substances like benzene, molten hypo (Sodium thiosulphate) naphthalene, phosphorous and antimony have similarly been cooled much below their freezing points. *The cooling of a liquid below its freezing point is called **super cooling** and the liquid in this condition is said to be super cooled.*

The phenomenon of super cooling does not really go against the fact that a liquid solidifies at a definite temperature, which is its freezing point. For, it is essentially an unstable phenomena, because the addition of the smallest quantity of the solid or even impurity like grit or dust particles or any mechanical disturbance such as shaking, stirring etc. is enough to start solidification.

An interesting case of super cooling is offered by sodium thio-sulphate known as hypo. If this is melted and a cooling curve obtained in the usual way, it is found that the temperature falls quite steadily for a considerable time, obeying Newtons' law of cooling. Suddenly solidification starts, and immediately a considerable rise of temperature takes place, temperature rising to, and remaining steady at the true melting point until all the hypo has solidified. It then starts to fall again according to the ordinary law of cooling as shown in Fig. 9.3. This case provides a very good example of the **latent heat** set free when a solid freezes. The super cooled liquid retains this heat until solidification occurs, but, at the moment freezing sets in, the latent heat is given up and a rise of temperature may be observed.

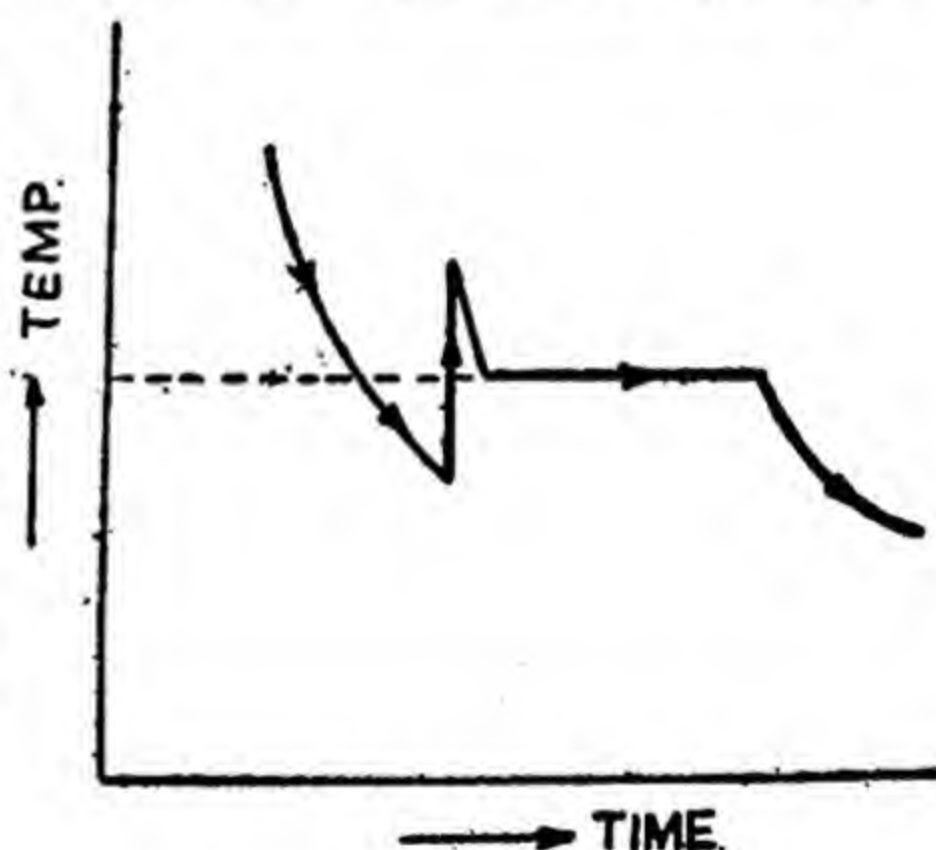


Fig 9 .3

9.6. Effect of pressure on melting point. The melting point of a solid is found to depend on external pressure. The effect is as follows.

Substances which contract on melting e.g., ice, iron and antimony etc. have their melting points lowered by increase of pressure, whereas those substances which expand on melting have their melting points raised e.g., paraffin wax, ghee, copper etc.

The magnitude of the change in the melting point due to changes in pressure can be calculated from the *Clausius Clapeyron equation*.

$$\frac{dP}{dT} = \frac{JL}{T(V_2 - V_1)}$$

Where dT = change in the absolute melting temperature T

dP = change in the applied pressure

V_1 = Specific volume of the substance in the solid state

V_2 = specific volume of the substance in the liquid state

and L = Latent heat of fusion.

From this relation it can be readily deduced that the melting point of a few substances which increase in volume on solidification or contract on melting like ice, iron, antimony is lowered by increase of pressure, as shown below.

In the case of ice $V_2 < V_1$, hence dP/dT is negative. It shows that with increase in pressure, melting temperature is decreased.

The melting point of most of the substances, which contract on solidification (or expand on melting) like wax, copper etc. is raised by increase of pressure as shown below.

In the case of wax, $V_2 > V_1$, hence dP/dT is positive, showing that when dP is positive dT is also positive. In other words, melting temperature of wax, increases with increase in pressure.

Calculation shows that in the case of ice, the melting point is lowered by about 0.0073°C per atmosphere increase of pressure, whereas in the case of paraffin wax, the melting point increases by about 0.04°C per atmosphere.

9.7. Regelation. The fact that the melting point of ice is lowered by the increase of pressure can be shown by the following experiment.

Press two pieces of ice together for a few seconds. On removing the pressure, the two pieces of ice stick to each other to form one piece. It is because the pressure lowers melting point of ice, so that the ice melts at the surface of contact. On releasing the pressure the melting point rises again and the water formed again solidifies resulting in the formation of one piece. *This phenomenon according to which ice melts when pressure is increased and again gets solidified when pressure is removed is called Regelation* (re-again : glare, freeze). It can be convincingly demonstrated by the following simple experiment. Take a slab of ice and rest it on two supports. Hang over the ice-slab a loop of copper wire from the ends of which heavy weights are suspended as shown. It is found that the wire passes completely through the solid ice-slab and falls down without cutting it into two pieces.

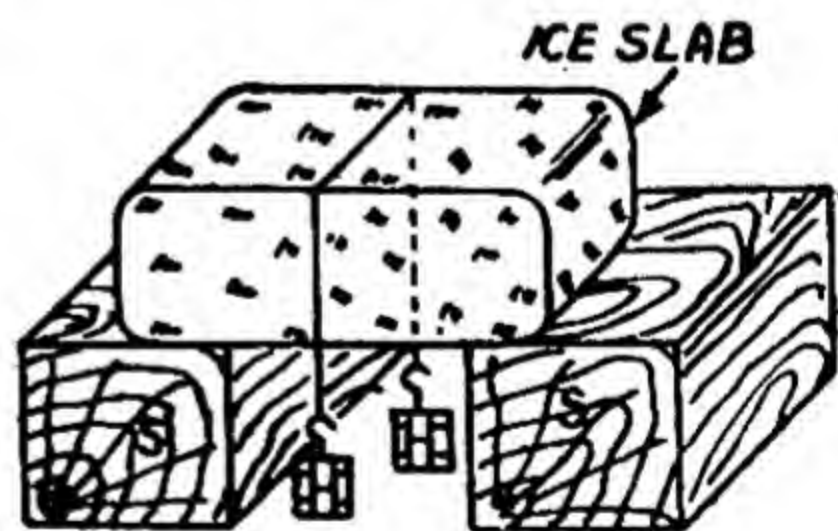


Fig. 9.4.

Explanation. The portion of the ice immediately below the wire is under increased pressure and, there, it melts. The latent heat necessary for melting is taken from the wire and the ice surrounding

it, and thus results in the fall of temperature of ice to a value below 0°C . The wire sinks through the water formed from melted ice and presses on a fresh part of ice which also melts under increased pressure. The latent heat for its melting is taken from the water above the wire, because this water being no longer under pressure, freezes as soon it comes above. During freezing, it gives out latent heat which passes through the wire to the ice below and melts it. This process continues until the wire cuts its way completely through the block of ice, leaving the block as a single united piece as if it had never been cut through.

It also follows that a metallic wire required for this purpose should be a good conductor of heat. Thus **copper wire** will cut its way through the block of ice more quickly than an iron wire of the same as iron is comparatively a poor conductor of heat.

Snow balls. can be made by pressing fresh snow with hands. The small pressure applied is sufficient to melt particles of snow inside and removal of pressure binds the particles of snow into a stable form of a ball. If, however the temperature of the snow is much below the freezing point, such balls can not be formed, since hand pressure is insufficient to cause melting. Figures in snow can be built on the same principle.

Skating. The edges of the skates, being very fine, exert a very large pressure on the ice which consequently melts. The water thus formed acts as a lubricant and enables the skates to glide along the ice. The edges usually sink far enough to enable them to "grip" the ice which would not be possible if the ice is very cold and this is why skates do not "bite" in very cold weather.

Glacier motion is also attributed to this phenomenon. The layer of ice at the bottom of glacier is subjected to a pressure due to its weight. The ice thus melts and water oozes out and resolidifies. *The block of ice thus moves continuously.*

Metal casting. An important practical application of metals that expand on solidification is made in solid casting. In order to obtain sharp casts from a mould, iron which expands on solidification is used. The casting in copper or silver is much less sharp because these metals contract on solidification.

9.8. Freezing Point of Solutions. When a substance is dissolved in a pure liquid, the substance is called the solute, the pure liquid is called the solvent and the resulting mixture is called the solution.

Experiment shows that *the freezing point of a solution is always lower than that of the pure solvent. This phenomenon is some times spoken of as the depression of the freezing point.* It was shown by **Blagden** that the lowering of the freezing point of a liquid is proportional to the concentration of the solute. This is known as **Blagden's Law**.

Later on it was found by **Rauolt** that for a given solvent, the *depression of the freezing point of its solution is proportional to the molar*

concentration of the solute irrespective of the nature of the solute dissolved. **Rauolt's Law** may be expressed in mathematical symbols in the form

$$\Delta T = KC$$

Where ΔT = Depression of the freezing point below that of the pure solvent.

C = Concentration of the solution in gram molecules of solute per 100 gm. of solvent.

K = Constant for given solvent and is known as cryoscopic constant. For substance dissolved in water the value of ΔT is about 18.5°C .

9.9. Mechanism of freezing mixtures. Any two substances which on mixing produce cooling constitute a freezing mixture. A mixture of ice and common salt (sodium chloride (NaCl)) is a good example of a freezing mixture. The fall in temperature is due to the following reason.

The ice first melts and takes the latent heat of fusion from the salt and the surrounding ice. The salt then dissolves in the melted ice and takes the heat of solution from the mixture and thus a fall of temperature takes place. When ice and common salt are mixed in proper proportion i.e., 3 : 1 by weight the temperature falls to about -23.6°C . This proportion of 3 : 1 is called the **eutectic proportion**.

Another mixture, commonly used is obtained by mixing calcium chloride crystals and ice in the proportion 3 : 2 by weight and thus produces temperature of -55°C .

By mixing solid carbon dioxide and ether in the proportion 4 : 1 by weight a temperature of -77°C can be obtained.

Let us consider in further detail the freezing of an aqueous solution of common salt (NaCl). When this dilute solution of common

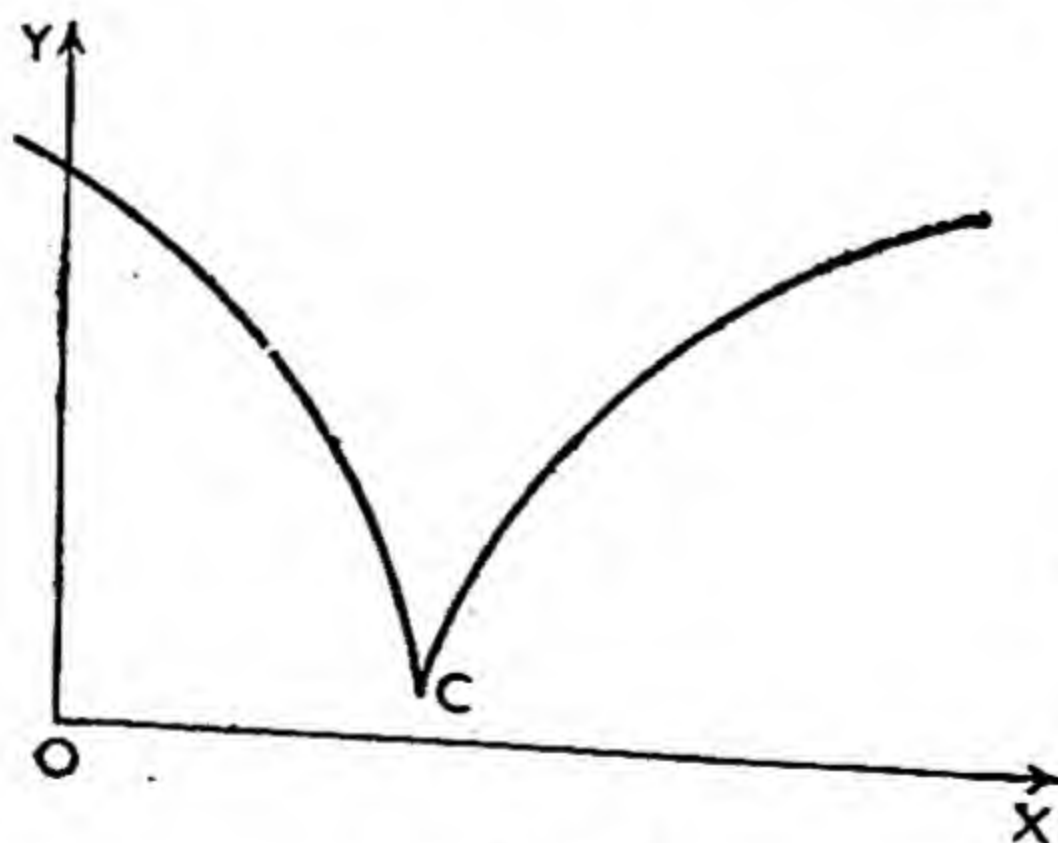


Fig. 9.5.

salt and water is cooled down to 0°C , it remains liquid. When

cooling is continued further between 3° and 4° below zero some pure ice separates from solution. This temperature at which ice first appears is called the **freezing point of the solution**. If the solution is further cooled then more ice is formed and the remaining solution becomes progressively richer in salt. This continues until a temperature of about -23°C is reached, when the whole of the remaining liquid freezes into a solid mass. This mass contains about 23.6 percent of salt. A solution containing 23.6% of salt is called a **eutectic mixture** and -23°C is called the eutectic temperature. This phenomenon is well explained by the freezing curves for ice and salt as shown in Fig. 9.5. The eutectic point at a temperature of -23°C and a concentration of 23.6% NaCl is clearly marked. To the left of C, the solid deposited on cooling is pure ice and to the right of point C, the solid which separated out is pure salt. At C both ice and salt are deposited together i.e., the mixture appears to solidify as a whole.

9.10. Alloys An alloy is a mixture of two or more metals, and, in general it has been found experimentally that the temperature at which an alloy melts is below the temperature of the lowest of the melting points of the constituents. In certain respects an alloy behaves as though it were a solution of one constituent in the other. The graph of the melting point of an alloy of copper and silver against the percentage of silver is shown in Fig. 9.6.

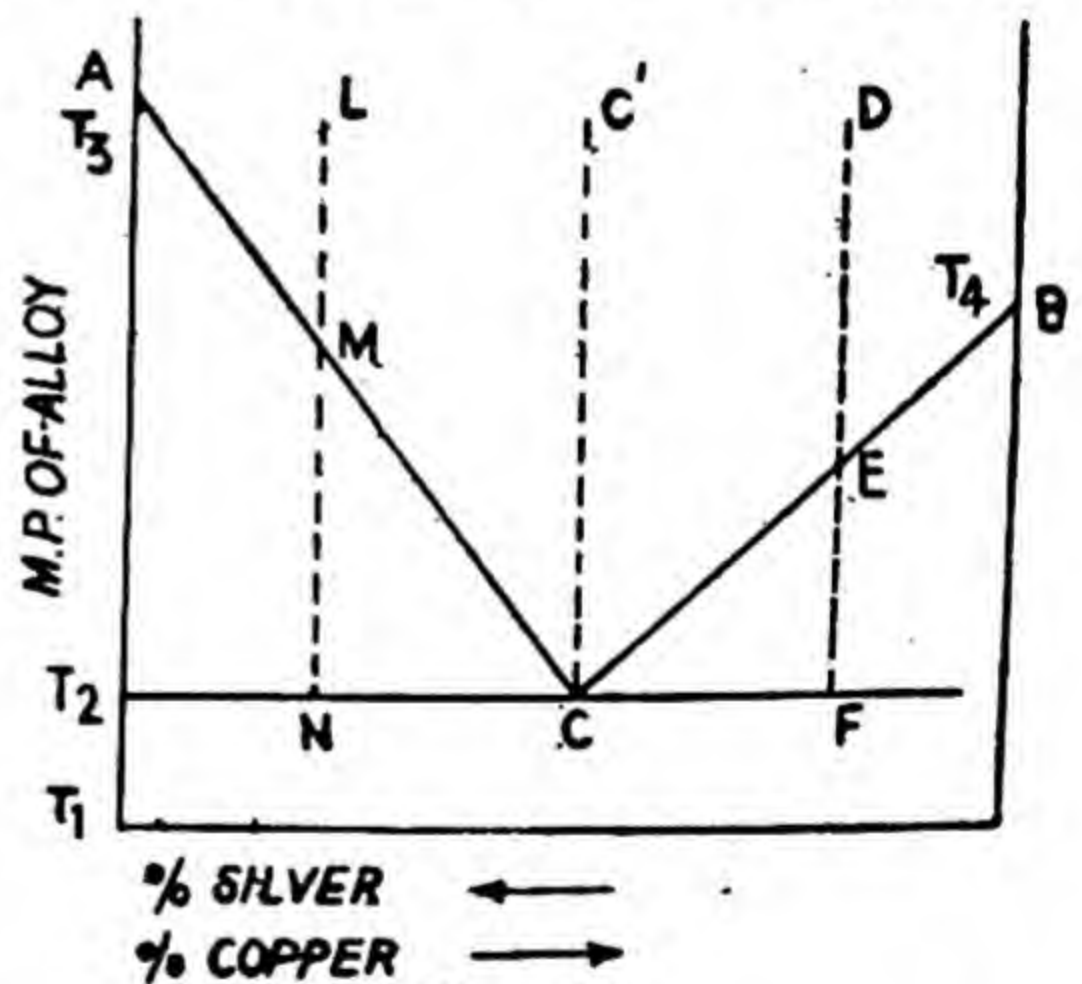


Fig. 9.6

Melting point of pure copper is 1083°C and is represented by point A. Similarly melting point of silver is 961°C as represented by point B. If to any one of these metals we go on adding increasing amounts of the other, the melting point of the resulting mixture goes on decreasing in a regular manner until it reaches a minimum value of 740°C as represented by the point C. The composition of the alloy at this temperature is 40% copper and 60% silver. The copper silver alloy of this composition is known as **Eutectic alloy** and the temperature of 740°C is called **Eutectic temperature**. Above this temperature either the copper or the silver crystallizes out, according to the percentage composition of the alloy, but below it the eutectic alloy freezes (solidifies) as one mass.

Consider an alloy containing 20% silver and 80% copper in the molten condition. If the temperature is decreased then as shown by

the vertical line LMN in Fig.9.6. it is copper and not silver that crystallises out at point M and continues to do so till N is reached.

At N the molten liquid left has the same eutectic composition i.e., 60% silver and 40% copper as at C . Below this temperature eutectic alloy freezes in this composition as one mass. If molten alloy contains 80% silver and 20% copper in the beginning then silver crystallises out first at the point E and continues to do so till F is reached. Again at F the molten liquid left has the eutectic temperature as at C . Below this temperature the eutectic alloy freezes enblock (as one mass). However if the molten alloy with eutectic composition is considered at a temperature represented by point C' and is cooled gradually then it remains in the liquid state all through and then freezes completely as C is reached without any previous solidification of either silver or copper. The eutectic points of some alloys having two metals in composition are given below.

Metals in the alloy	M. Point ($^{\circ}C$) 1st metal	M. Point ($^{\circ}C$) 2nd metal	Eutectic point ($^{\circ}C$)
1. Copper and silver.	1083	981	740
2. Lead and Tin.	327	232	186
3. Antimony and lead.	630	327	246

Example 1. How much heat is required to convert 20 gms. of ice at $-30^{\circ}C$ into steam at $100^{\circ}C$.

Latent Heat of steam = 536 cal./gm. and latent heat of fusion of ice 80 cal./gm. specific heat of ice = 0.5 cal./gm./ $^{\circ}C$.

Heat is required as follows.

(a) Heat required to raise the temp. of ice from $-30^{\circ}C$ to $0^{\circ}C = mSt$

$$= 20 \times 0.5 \times [0 - (-30)] \\ = 20 \times 0.5 \times 30 = 300 \text{ cal.}$$

(b) Heat required to convert ice into water

$$\text{at } 0^{\circ}C = mL \\ 20 \times 80 = 1600 \text{ cal.}$$

(c) Heat required to raise the temperature of water from $0^{\circ}C$ to $100^{\circ}C = mS\theta$

$$= 20 \times 1 \times (100 - 0) \\ = 2000 \text{ cal.}$$

(d) Heat required to convert water into steam

$$\text{at } 100^{\circ}C = mL' \\ = 20 \times 536 \\ = 10720 \text{ cal.}$$

$$\begin{aligned}
 \text{Total Heat required} &= a + b + c + d \\
 &= 300 + 1600 + 2000 + 10,720 \\
 &= 14620 \text{ cal.} \\
 &= 14.62 \text{ Kilo-cals.}
 \end{aligned}$$

9.11. Boiling. When a liquid, such as water originally at room temperature is heated in an open vessel, and when temperature has risen sufficiently, bubbles may be seen rising from the bottom of the vessel. The bubbles frequently contain some air together with the vapour of the liquid. It is most improbable that a bubble should form in the body of the liquid unless some foreign material such as a dust particle, happen to be present. At relatively low temperatures the bubbles cannot increase in size since the sum of the bubbles is less than the hydrostatic pressure due to the atmosphere and the liquid. Hence they keep clinging to the walls of the vessel and cannot rise up to the liquid surface. As the temperature rises, a point is reached due to the rapid increase of vapour pressure with temperature when the total pressure inside the bubbles is equal to or just exceeds the external pressure. The bubbles will now grow in size and with further evaporation they will become too big and buoyant to remain attached to the sides of the vessel. They then collapse away and rise to the surface in quick succession. As the temperature is increased further, more bubbles are formed which contain mostly liquid vapours instead of air. They also rise to the top of the liquid and then escape into the air.

As the temperature rises, further bubbles of steam appear at the bottom and begin to rise to the surface. Since the upper layers are colder than the lower layers, these bubbles condense producing sharp clicks which has a characteristic sound called the *singing of the kettle*. With the rise of temperature bubbles of steam cease to condense, the singing sound stops and the vapours begin to escape rapidly into the air. Since these bubbles do not collapse (break) on rising to the surface, it is obvious that the pressure of the vapour inside them must be equal to the atmospheric pressure. The liquid is now said to be boiling or in a state of ebullition. Thus it follows that a *liquid will boil at a temperature at which its maximum vapour pressure becomes equal to the pressure acting on its free surface*. It is for this reason that the boiling point of a liquid is also defined as *a temperature at which its maximum vapour pressure becomes equal to the external pressure acting on its surface*. The experiment shows that the maximum vapour pressure of water at 100°C is 76 cm. of mercury which shows that water will boil at 100°C if the external pressure is 76 cm. of mercury.

The temperature of water remains constant so long as boiling continues. In a similar way all liquids when heated to a suitable temperature begin to boil. The constant temperature at which a liquid boils is called as its **boiling point**. The boiling point of a liquid remains constant if the pressure on its surface does not change.

Thus boiling or ebullition is a rapid change from liquid to the gaseous state. It takes place throughout the mass of the liquid at a definite temperature called its **boiling point**.

Boiling with bumping. When air-free water is heated in a glass vessel which has previously been carefully cleaned with hydrofluoric acid and then rinsed with water, it is possible to raise the temperature considerably above the normal boiling point without ebullition taking place. Indeed, by a process of alternate boiling and cooling to expel dissolved air, it has been found possible to raise the temperature of water to 105°C or 106°C . If more care is taken then water may boil at a still higher temperature. This is called **superheating** and this phenomenon of superheating like supercooling is unstable.

As soon as the temperature of the superheated liquid becomes high enough for bubbles to form, these will grow very rapidly, and a large amount of vapour may be given off with almost explosive violence. This is called bumping. However, the moment this bumping starts, the temperature at once falls to the normal boiling point. This phenomenon is known as **boiling with bumping**, for the boiling is both violent and intermittent in character.

To prevent bumping, it is customary to introduce into the vessel some fragments of porous material or small pieces of capillary tubes, which probably carry with them surface layers of condensed gas or other impurity. Sand or iron filings have the same effect.

Effect of surface tension in the formation of bubbles. The formation of bubbles in a liquid and the complementary case, the formation of liquid drops in a vapour are closely related to surface tension of the liquid. It is well known that a liquid surface behaves in many respects like an elastic membrane, and tends to contract so as to make the surface area and the corresponding potential energy as small as possible.

When air bubble exists in a liquid, this tension tends to make the bubble contract until the forces of contraction are balanced by a force produced by the pressure within. If the surface tension is T , and the radius of bubble is r , the edges of the two hemispheres composing the surface are pulled together by a force $2\pi rT$. The counteracting force due to the excess pressure P inside is $P\pi r^2$, for it may be estimated across the equatorial section of area πr^2 .

$$\text{In equilibrium} \quad P\pi r^2 = 2\pi rT$$

or

$$P = 2T/r$$

This shows that for a given value of T the pressure difference is very large when the bubble is very small. When the bubble grows in size sufficiently, then r is large, hence $2T/r$ becomes small and plays no significant part. If there is sufficient air present in the cracks and crevices in the sides of the vessel, then air bubbles of appreciable size are formed right from the start. Since the initial radius r is large, the term $2T/r$ is negligibly small, so that surface tension plays no significant part in the boiling of the liquid.

Laws of Ebullition or Boiling. (i) Every liquid begins to boil at a certain fixed temperature called its boiling point.

(ii) At boiling point, the saturation or maximum vapour pressure of the liquid is equal to the pressure acting on the surface of the liquid.

(iii) From the moment boiling begins, the temperature remains constant till the whole of the liquid has boiled off.

(iv) Every liquid begins to boil at a certain temperature which differs from liquid to liquid but depends on the pressure acting on the surface of the liquid.

(v) The boiling point is raised by the increase of pressure and lowered by the decrease of pressure on the liquid surface.

(vi) A unit mass of each liquid requires a definite amount of heat to change it from the liquid to the gaseous state without change of temperature. This amount of heat is known as *latent heat of vaporisation*.

(vii) There is enormous increase in volume when a liquid changes to the gaseous state. For example, when one c.c. of water is converted into steam it occupies about 1600 c.c.

9.12. Determination of Boiling point. Boiling point of a liquid is that temperature at which the maximum pressure of the vapour is equal to the atmospheric pressure. In other words it means that a liquid in communication with the atmosphere boils at a temperature such that the saturated vapour pressure at that temperature is equal to the atmospheric pressure. This forms the basis of a simple laboratory method for finding the boiling points of various liquids. Fig. 9.7, shows a piece of apparatus which is designed to illustrate this fact.

A *J*-shaped glass tube is closed at the top of the short limb, the other limb being open to the atmosphere. The bend of the tube contains mercury. The space above the mercury in the closed limb is completely filled by a short column of water. The air in that space is expelled out before introducing water. The *J* tube along with a stirrer and a sensitive thermometer is placed in a beaker of oil or water. If we heat this shorter limb, we shall find that when the temperature reaches the boiling point, the pressure of the vapour arising from this water is sufficient to depress the mercury so that it stands

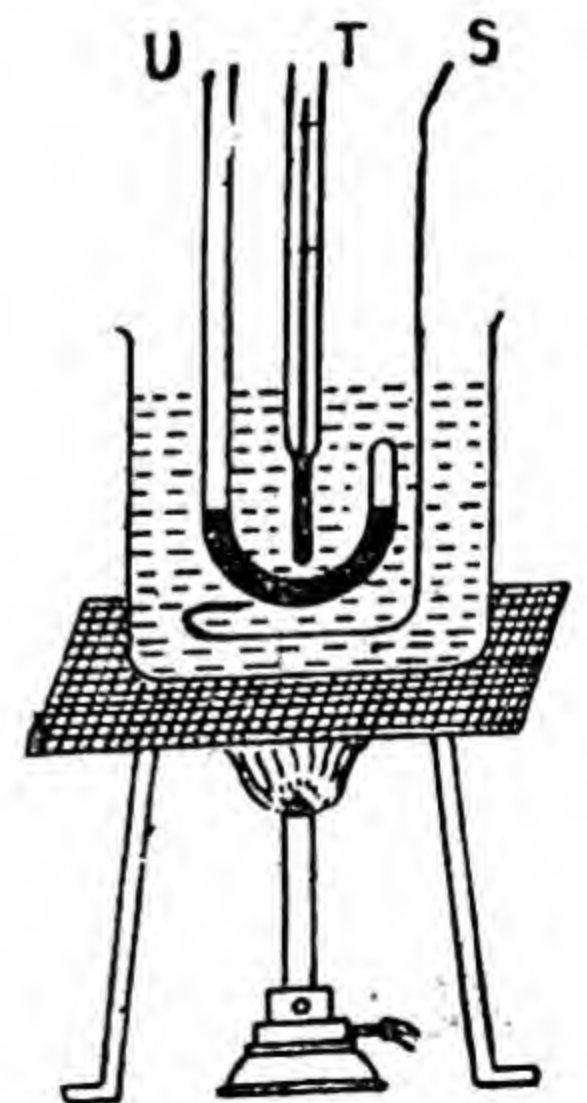


Fig. 9.7

at the same level in both limbs of the tube as illustrated in the figure. This shows that the pressure of the vapour inside is equal to the atmospheric pressure. This temperature is noted and is the boiling point of the liquid.

The temperature is further raised so as to heat the liquid a few degrees beyond its boiling point and is then allowed to cool. The temperature at which condensation takes place is also noted. The mean of these two readings gives the boiling point of the liquid. This experiment is not very easy to carry out because of the possibility of traces of air being present in the closed limb.

This apparatus also affords a convenient laboratory method of determining the boiling points of other liquids such as ether and alcohol.

Boiling point of solutions. Similar to the case of freezing point of solutions, the boiling point also is affected by the process of solution. *The boiling point of a solution is higher than that of the pure solvent.*

Solutions obey the same law of boiling as pure liquids *viz.*, the saturated vapour pressure of the liquid at its boiling point is equal to the atmospheric pressure; but there is an important difference, *viz.*, the vapour pressure of a solution at a given temperature is always less than that of a pure solvent at the same temperature. Thus the vapour pressure of a salt solution at 110°C is less than 76 cm., hence the salt solution has to be heated to a temperature higher than 100°C for its vapour pressure to reach the value of the atmospheric pressure when boiling will set in.

The elevation of the boiling point of solution is found to be proportional to the concentration of the solute. Raolt's Law which applies to the depression of the freezing point also holds good for the elevation of the boiling points for aqueous solutions of non-electrolytes and solutions of organic compounds.

The law states that

$$\Delta T = KC$$

where ΔT is the elevation *i.e.*, increase of the boiling point, C the concentration of the solution in gm-molecule of the solute per 100 gm of solvent and K a constant for the solvent whose value is 5.2°C for aqueous solutions.

9.13. Effect of pressure on boiling point. From what has been discussed about the vapour pressure of a liquid at its boiling point, it follows that if the external pressure on the liquid is altered, the liquid will boil at a different temperature at which the vapour pressure will be equal to the new external pressure. Hence an increase of pressure raises the boiling point of a liquid and a decrease lowers it. The magnitude of the change in boiling point due to an increase in pressure is given by the Clausius-Clapeyron

thermodynamical relation.

$$\frac{dP}{dT} = \frac{JL}{T(V_2 - V_1)}$$

where dP = change in pressure

dT = rise in boiling temperature in $^{\circ}K$

V_1 = specific volume of the liquid

V_2 = specific volume of the vapour

T = boiling temperature in $^{\circ}K$

J = Mechanical equivalent of heat

L = Latent heat of vaporisation.

It will be seen that when a liquid passes from the liquid state to the vapour state at the boiling point, $V_2 > V_1$. Thus $\frac{dP}{dT}$ is a positive quantity which means if dP is positive, dT is also positive.

9.14. The triple point. *The triple point may be defined as the point where the three states of matter i.e., solid, liquid and vapour co-exist in equilibrium. It lies at the junction of steam line, ice line and hoarfrost line.*

Imagine a cylinder fitted with a gas tight piston and filled with a substance partly in the liquid state and partly in the state of saturated vapour at a certain temperature. Then by Dalton's Law the pressure P is a function of the temperature alone $P = f(T)$. This means that at a particular temperature T , and under corresponding pressure P the liquid and its vapour are in equilibrium when in

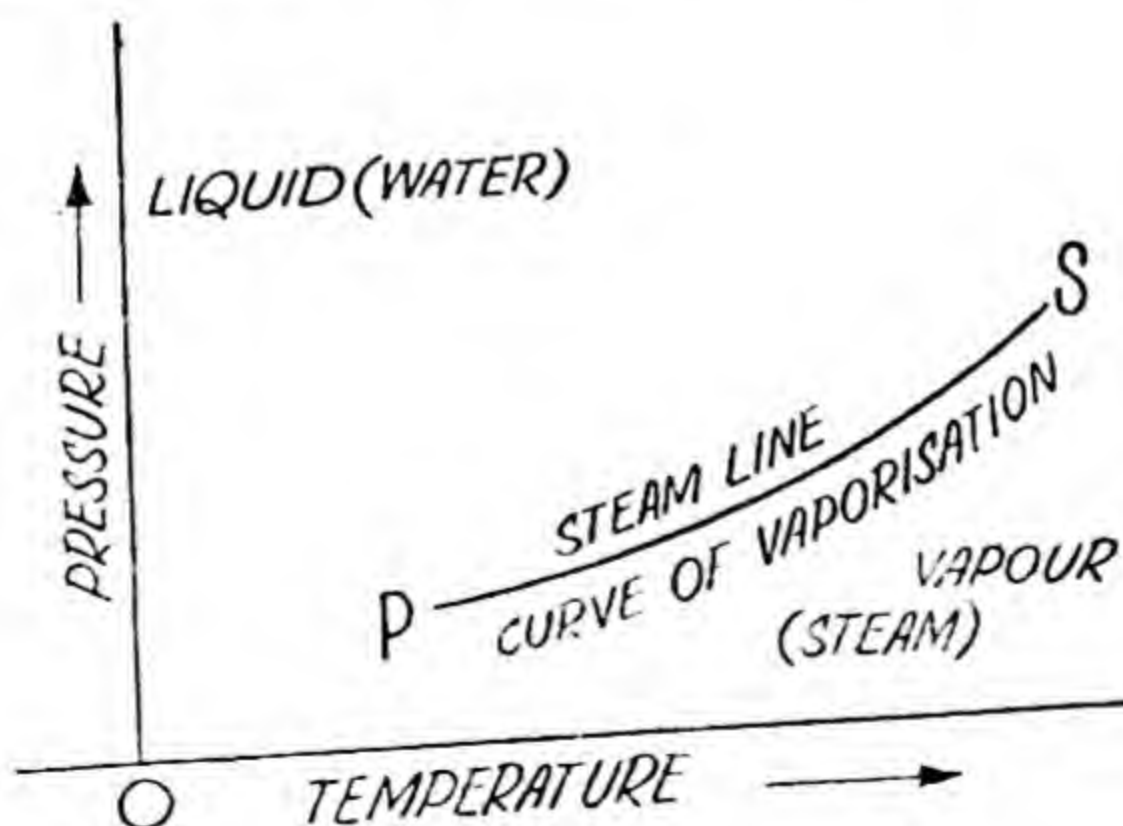


Fig. 9.8

contact. The relation between pressure and temperature may be represented by a graph, taking pressure as the ordinate and temperature as the abscissa as shown in Fig. 9.8. ✓

When the temperature of the system is changed, the saturation vapour pressure is also changed. If a graph is plotted between maximum vapour pressure and temperature a curve of the type PS as shown in Fig. 9.8 is obtained. This curve is called the curve of **vaporisation** or **steam line** in case of water and steam. All points on the curve PS correspond to an equilibrium state between liquid and vapour.

For any point above the line the substance is entirely in the liquid state and for any point below the line the substance is entirely in the vapour state. A liquid and a solid similarly exist together in equilibrium at the temperature at which the solid melts under a given pressure. This pressure is also a function of temperature only, and relation between pressure and temperature is represented by the curve PI as shown in Fig. 9.9. It is called the curve of fusion or **ice line** in case of ice and water. We have seen in connection with the change of state from solid to liquid that the substances may be divided into two classes as given below.

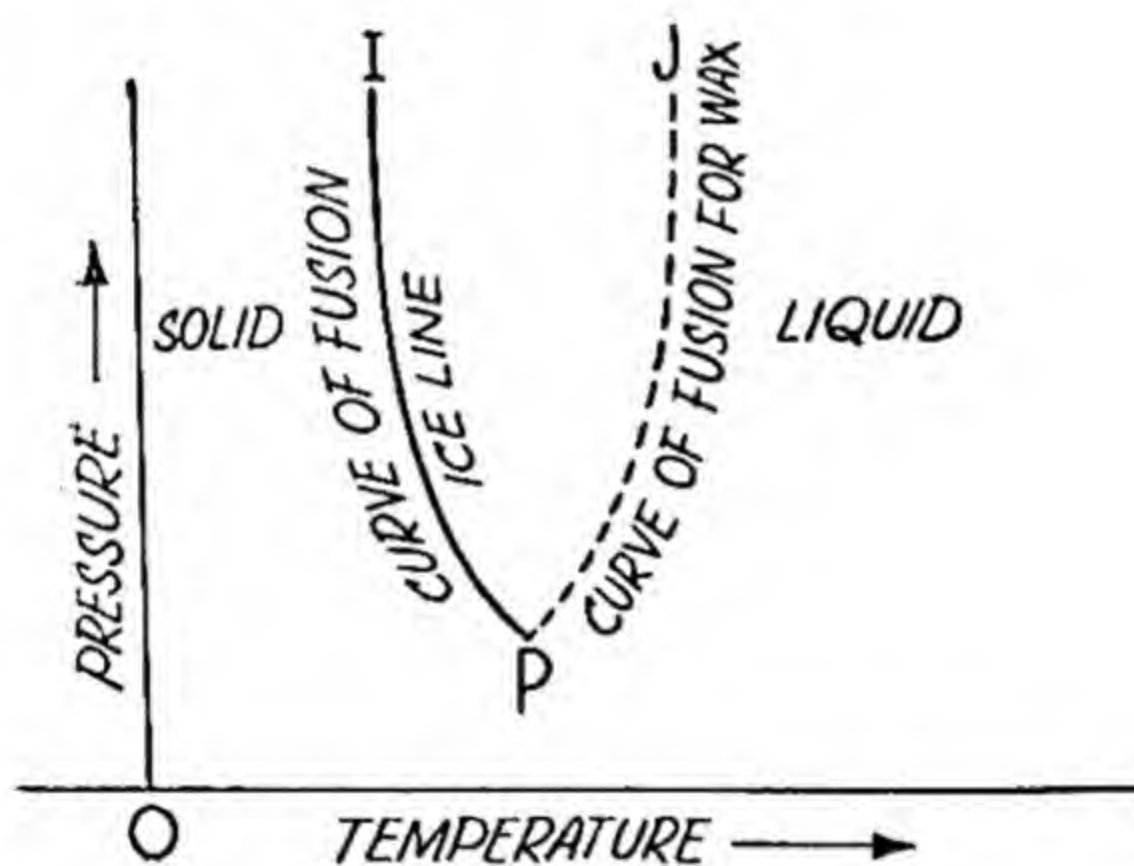


Fig. 9.9.

(i) Those which *expand on solidification e.g. ice*. In such a case the melting point is lowered by increase of pressure. This case is represented by the curve PI which slopes towards the left. (ii) Those which *contract on solidification e.g., wax*. In such a case the melting point is raised by increase of pressure. This case is represented by the dotted curve PJ which slopes towards the right.

In the third place, a state of equilibrium may exist between a solid, such as ice and its vapour. The graph representing the relation between pressure and temperature of a substance partly in the solid and partly in the vapour state is called the curve of **sublimation** or **hoarfrost line** HP in case of ice as shown in Fig. 9.10.

When all these three curves are drawn on the same diagram

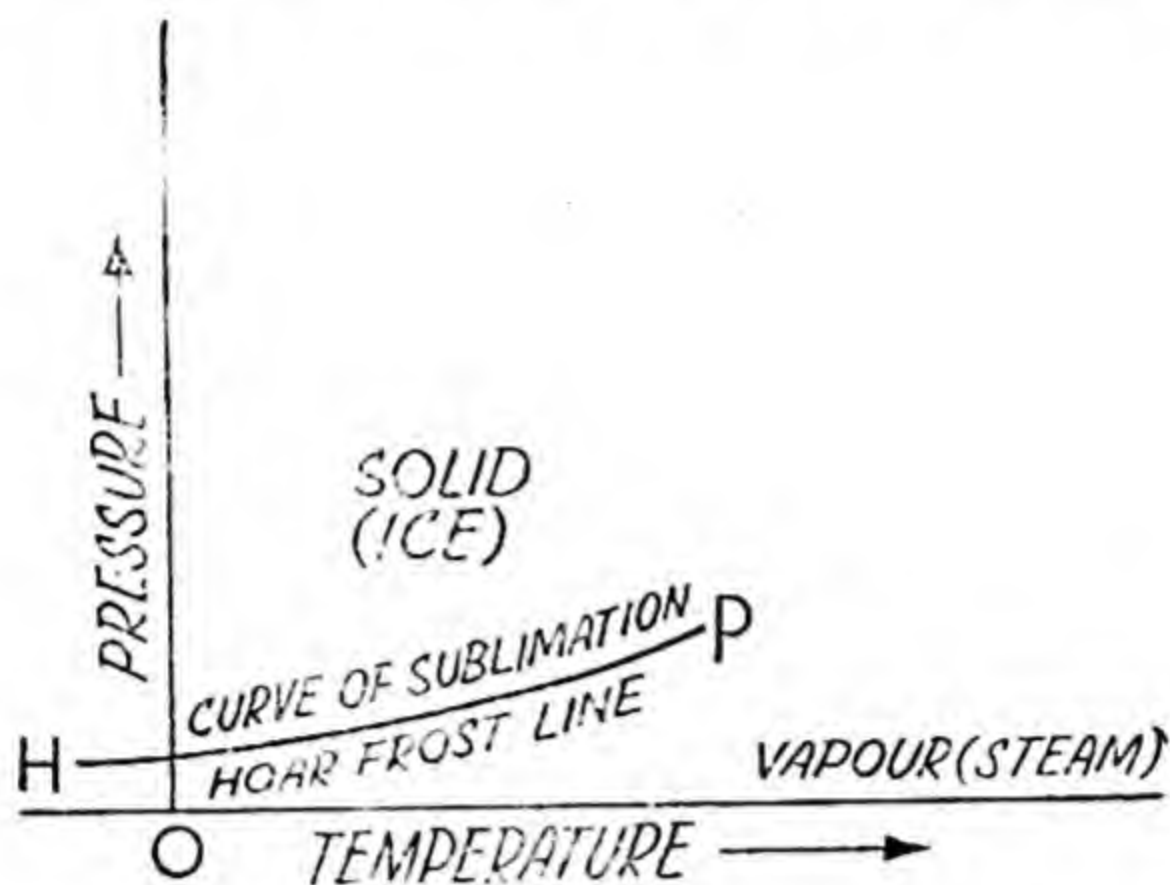


Fig. 9.10.

they meet in a single point P , called the **triple point** or the fundamental point as shown in the Fig. 9.11.

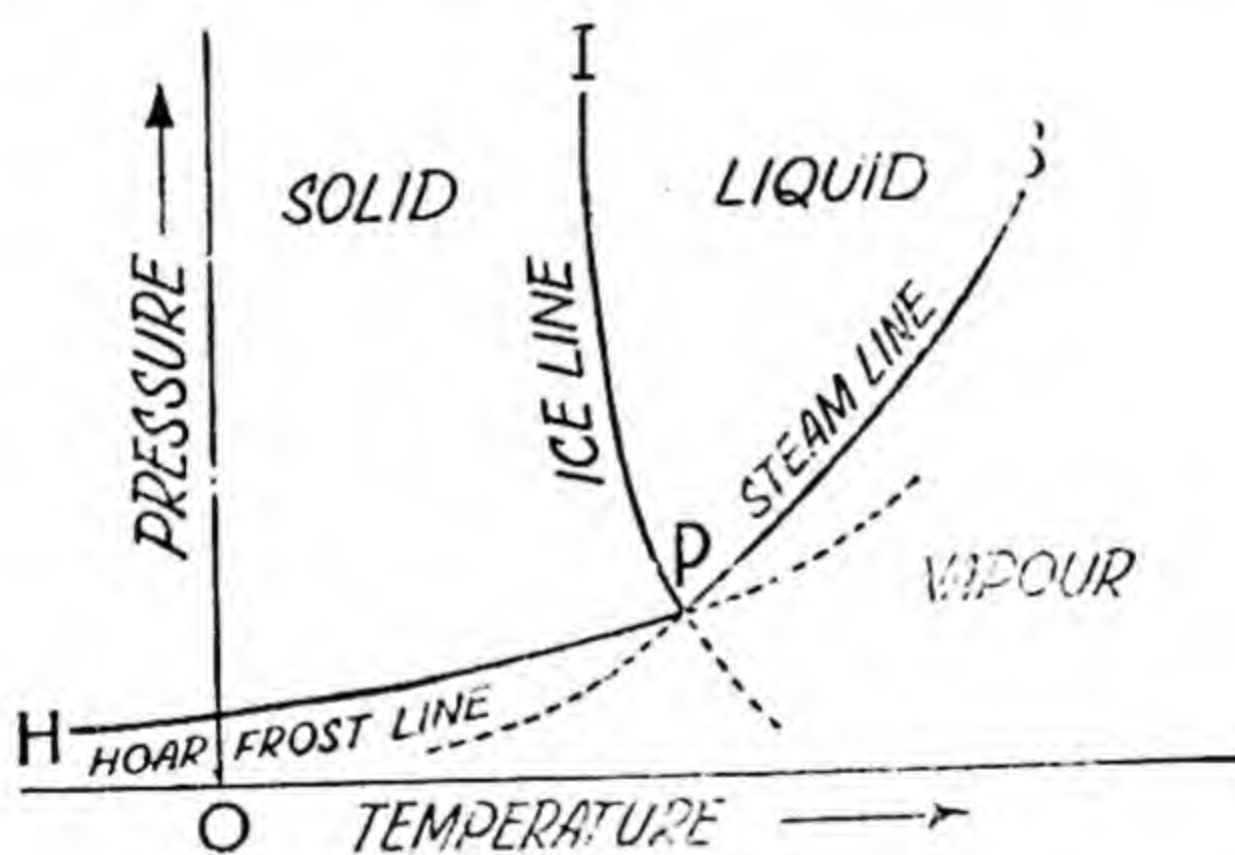


Fig. 9.11.

It may now be defined as the point where, for a particular temperature and pressure solid, liquid and vapour exist simultaneously in the same space in equilibrium without any change in their relative proportion. Thus triple point is independent of pressure. We may further observe that the three curves are not only the curves of equilibrium of the three states, but in addition they mark the boundaries of the three states on the P - T diagram. The substance is entirely in the solid state in the region HPI , entirely in the liquid state in the region IPS and entirely in the vapour state in the region below the line HP and PS .

The triple point of a substance like ice which expands on solidification is above its melting point at normal pressure and the substance cannot exist in the solid state above the triple point. The triple point of a substance like wax which contracts on solidification

is below its melting point under normal pressure and the substance cannot exist in the liquid state above the triple point.

Numerical values for water at the triple point. At the triple point the pressure of the saturated vapour is equal to the pressure of fusion and it is also equal to the pressure of sublimation. The temperature is slightly above 0°C . At 0°C the maximum vapour pressure of water is 4.6 m.m.

The specific volumes of water in the three states at the triple point are 206000 c.c. (vapour). 1 c.c. (water) ; 1.09 c.c. (ice). Regnault thought that the hoar-frost line was a simple continuation of the steam line, but it was shown by Kirchhoff that they are two distinct curves meeting at an angle. The direction of each curve at the triple point may be found by calculating the value of $\frac{dP}{dT}$ by applying thermodynamic principles.

9.15. Vapour pressure over curved surfaces. Due to surface tension the pressure of a saturated vapour in equilibrium with its liquid is not the same when the liquid surface is curved and when it is plane.

An expression for the vapour pressure over a curved liquid surface can be obtained as follow. A capillary tube is placed vertically in a liquid and the whole is enclosed in a vessel from which air has been exhausted so that the space above the liquid is filled with its vapour and with nothing else. In general, the liquid in the capillary tube stands at a higher level A than the level B and its surface is curved (concave upwards) as shown in Fig. 9.12.

There is a state of equilibrium between the liquid and its vapour both at A and B , otherwise evaporation or condensation will occur until equilibrium is reached. We will assume that the temperature is constant.

Let p_0 = vapour pressure in contact with the plane surface that is, the pressure at B .

p = Vapour pressure just outside the liquid at A i.e. A'

p_1 = the pressure just inside the liquid at A i.e. A''

ρ = the density of the liquid.

σ = the density of the vapour (assumed constant)

The pressure at B exceeds that at A due to the column of the vapour of height AB . Let this height be h , then

The pressure exerted by a column h of the vapours of density σ is $h\sigma g$

\therefore

$$p_0 - p = h\sigma g$$

...(i)

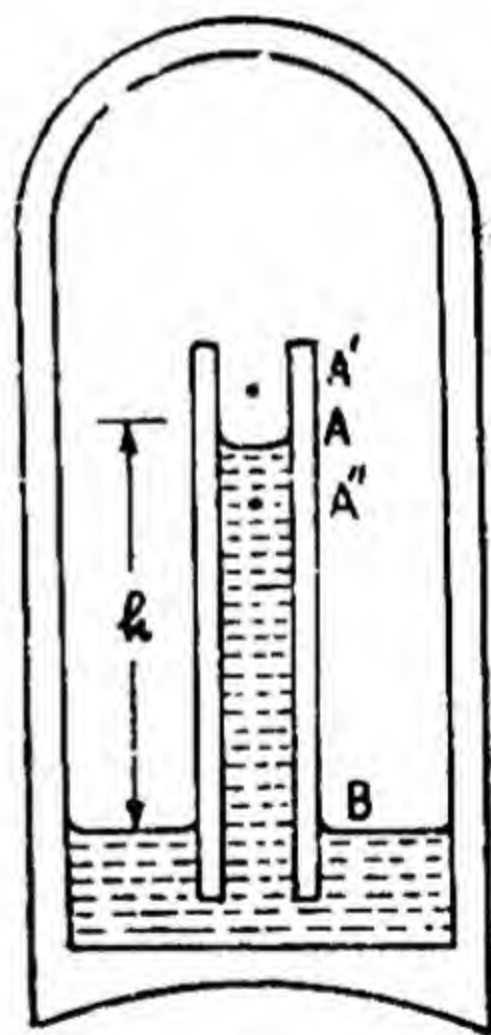


Fig. 9.12

The pressure due to a column h of the liquid of density ρ is $h\rho g$

$$\therefore p_0 - p_1 = h\rho g \quad \dots(ii)$$

The curvature of the liquid surface in a capillary tube is due to the surface tension T . The difference in pressure across this concave surface *i.e.*, the pressure difference between the inside and the

outside of the surface at A is equal to $\frac{2T}{r}$ where r is the radius of curvature of the surface at A .

$$\therefore p - p_1 = \frac{2T}{r}$$

Subtracting (i) from (ii) we have,

$$p - p_1 = gh(\rho - \sigma)$$

$$\therefore \frac{2T}{r} = gh(\rho - \sigma)$$

$$\text{or } gh(\rho - \sigma) = \frac{2T}{r} \quad (iii)$$

If we substitute this value of gh in equation (i) we have

$$p_0 - p = \sigma \frac{\frac{2T}{r}}{\rho - \sigma}$$

$$\text{or } p = p_0 - \frac{\sigma}{\rho - \sigma} \cdot \frac{2T}{r} \quad \dots(iv)$$

This shows that the vapour pressure in contact with a concave surface is lower than that in contact with a plane surface by an amount $\frac{2T}{r} \cdot \frac{\sigma}{\rho - \sigma}$ depending on the radius of curvature r of the surface.

Similarly if the surface is convex towards the liquid then the above expression becomes.

$$p - p_0 = \frac{2T}{r} \cdot \frac{\sigma}{\rho - \sigma}$$

$$\text{Hence } p = p_0 + \frac{2T}{r} \cdot \frac{\sigma}{\rho - \sigma}$$

Thus the vapour pressure in equilibrium with a convex liquid surface is greater than for that a plane surface by an amount $\frac{2T}{r} \cdot \frac{\sigma}{\rho - \sigma}$. Representing the difference in vapour pressure over plane and

curved surface by Δp , we have

$$\Delta p = \frac{2T}{r} - \frac{\sigma}{\rho - \sigma}$$

From the above expression it is clear that the pressure difference Δp varies inversely as the radius r of the curved surface. This fact has important bearing on the phenomenon of *boiling* and *formation of clouds*.

(i) **Boiling.** In the process of boiling, if there are nuclei of sufficiently large radii due to the presence of dust particles or iron filings or of porcelain bits placed in the liquid, the bubbles formed round these nuclei are fairly big, so that the excess pressure due to surface tension is of moderate amount and the vapour pressure can easily support it along with the hydrostatic pressure, thereby leading to the normal and regular boiling.

If on the other hand, there are no or very small nuclei present, the excess of pressure due to surface tension will be extremely large, so that the vapour pressure at the formation of bubbles cannot support it and this will lead to superheating where the equilibrium between vapour pressure and hydrostatic pressure will be very unstable with the consequent boiling by bumping.

(ii) **Formation of Clouds.** Dust particles and charged ions play an important part in inducing the condensation of water vapour in the atmosphere in the form of clouds, fog and mist etc. This can be explained in the following manner. Clouds, fogs and mists are aggregates of minute water drops, which in general are found round dust particles. These act as nuclei of appreciable radii of curvature, so that super saturation pressure Δp , due to the cooling of the atmosphere loaded with water vapour have not to be so large as under dust free conditions. Hence presence of nuclei in the atmosphere because of dust particles or charged ions favour the formation of clouds, mists and fogs with comparative ease. In the absence of such nuclei, no clouds or mists would have been formed even if the atmosphere is saturated with water vapour and cooled to a temperature lower than the dew point.

Example 2. A closed vessel contains a mixture of air and water vapour in contact with excess of water. The pressure in the vessel at 27°C and 60°C are respectively 77.7 and 98.1 cm of mercury. If the vapour pressure of water at 27°C is 2.7 cm. of mercury, what is the vapour pressure at 60°C ?

The pressure of the air at $27^\circ\text{C} = 77.7 - 2.7 = 75.0$ cm,

The pressure of the air at $60^\circ\text{C} = 98.1 - p$,

where p is saturated vapour pressure of water at 60°C . Since the pressure of the gas at constant volume is proportional to its absolute temperature, we have for the constant mass of air in the mixture.

$$\frac{98.1 - p}{75.00} = \frac{273 + 60}{273 + 27}$$

$$\text{or} \quad 98.1 - p = \frac{333}{300} \times 75.00.$$

$$\therefore \quad p = 14.85 \text{ cm.}$$

Example 3. What mass of ether at 0°C must be evaporated in order to freeze 5 grams of water at 0°C ? The latent heat of vaporization of ether is 95 cal/gm. and that of water is 80 cal/gm.

Mass of water to be frozen, $m = 5$ gms.

Temperature of water $= 0^\circ\text{C}$.

Latent heat of water $L = 80$ cal/gm.

Heat lost by water to form ice $= mL = 5 \times 80 = 400$ cal.

Let the mass of ether evaporated to produce enough cooling to freeze 5 gms of water at 0°C be M gms.

Latent heat of vaporization of ether $= 95$ cal/gm.

Heat gained by ether $= M \times 95$ cal.

But, Heat gained $=$ Heat lost.

$$\therefore \quad M \times 95 = 400$$

$$\text{or} \quad M = \frac{400}{95} = 4.2105 \text{ gms.}$$

Example 4. A calorimeter weighing 40 gms (specific heat 0.1) contains 50 gms of water mixed with 50 gm of ice. Dry steam at 100°C is passed into the mixture until the temperature rises upto 10°C . What is the mass of the steam condensed? Latent heat of fusion of ice is 80 calories per gm. Latent heat of steam $= 540$ cal/gm.

Initial temperature of ice and water $= 0^\circ\text{C}$.

In the first stage all ice melts from ice at 0°C to water at 0°C . Then the whole mass of water (including that formed by melting of ice) gets heated up to 10°C .

$$\text{Heat required for this purpose} = (50 \times 80) + (50 + 50) \times 10 = 5000 \text{ cal.}$$

Heat required by the calorimeter to be heated from 0°C to 10°C .

$$ms t = 40 \times 0.1 \times 10 = 40 \text{ cal.}$$

$$\text{Total heat absorbed} = 5000 + 40 = 5040 \text{ cal.}$$

Let M be the mass of steam condensed for supplying the above quantity of heat.

This amount of steam condenses from 100°C to water and then cools down to 10°C water.

$$\begin{aligned} \therefore \text{Heat given out by } M \text{ gm. of steam.} \\ &= ML + M(100 - 10) \text{ cal.} \\ &= M \times 540 + M(90) \text{ cal.} \\ &= M(540 + 90) = 630 M \text{ cal.} \end{aligned}$$

$$630 M = 5040$$

Now

$$M = 5040 / 630 = 8 \text{ gms,}$$

\therefore

9.16. Vaporisation. When a liquid is heated it changes into vapour form. The change from the liquid to a vapour state is called **vaporisation**. The reverse phenomenon i.e., change of vapour into the liquid state is called **liquefaction** or **condensation**. Vaporisation may take place in two ways.

(i) *Evaporation.* In this process there is a slow formation of vapours at all temperatures and takes place only at the surface of the liquid. The gaseous state of the liquid is called the *vapour*. The liquids which readily evaporate are said to be volatile and those which do not evaporate at ordinary temperature are called non-volatile.

(ii) *Ebullition or Boiling.* In this process, there is a rapid formation of vapours from all parts of the liquid and at a constant temperature.

Factors favouring evaporation. The rate of evaporation is found to depend on a number of factors.

(i) **The nature of the liquid.** The lower the boiling point of a liquid, the quicker is the rate of evaporation. If the liquid, is more volatile the evaporation will be rapid. For example, alcohol evaporates more rapidly as compared to water and ether still more rapidly than alcohol.

(ii) **The area of the exposed surface.** As a general rule the larger the free surface of the exposed liquid more rapid is the evaporation. Thus if we take equal quantities of water in a wide dish and in a bottle, we find that water in the dish evaporates much earlier. It is for this reason that volatile liquids are kept in a narrow necked bottle which is corked tightly.

(iii) **The temperature of the liquid and air.** If the liquid is at a higher temperature, it will obviously get vaporised quickly.

(iv) **The renewal of air in contact with the liquid surface.** The layers of air above the surface of a liquid become almost saturated with vapour in a short time and hence these cannot absorb more vapour. Thus if air is not renewed, the evaporation will stop. If the layer of air in contact with the liquid is removed quickly, the evaporation becomes very quick. This is why evaporation is more rapid on a windy day than on a calm (still) day when no wind is blowing.

(v) **The pressure on the surface of the liquid.** The lesser the pressure on the liquid surface, the lower is the boiling point and hence quicker is the evaporation. Thus in vacuum, the evaporation is extremely rapid.

(vi) **The dryness of air.** The drier the air, the greater is the amount of moisture required for its saturation and, therefore, the quicker is the evaporation. It is for this reason that wet clothes dry more quickly on a dry day than on a rainy day.

9.17. Vapour and gas. In general a vapour is the gaseous condition of a substance which is liquid at ordinary temperature. The vapour can...

be liquified only by the increase of pressure without lowering its temperature, *e.g.*, water vapour, alcohol vapour etc. On the other hand a **gas** is that, to liquify which pressure on it has to be increased and also its temperature has to be lowered *e.g.* oxygen, hydrogen etc.

For every substance in the gaseous state there is certain temperature below which it can be liquified by suitably increasing the pressure, but above which it cannot be liquified however great the pressure may be. This temperature is known as **critical temperature** for that substance. Hence *in true sense a vapour is a gas above its critical temperature and gas is a vapour below its critical temperature*. For example, carbon dioxide should be called as a vapour at its room temperature (25°C) because its critical temperature is 31°C .

9.18. Vapour pressure. As already described, a liquid gives off vapour from its free surface at all temperature. As a vapour is also the gaseous state of liquid, it is expected to exert pressure in the same way as a gas does. A vapour actually exerts pressure can be proved by the following experiment.

Experiment. Take two barometer tubes *A* and *B* each about one metre long and from 0.5 to 1 cm. in diameter. Fill them with pure and

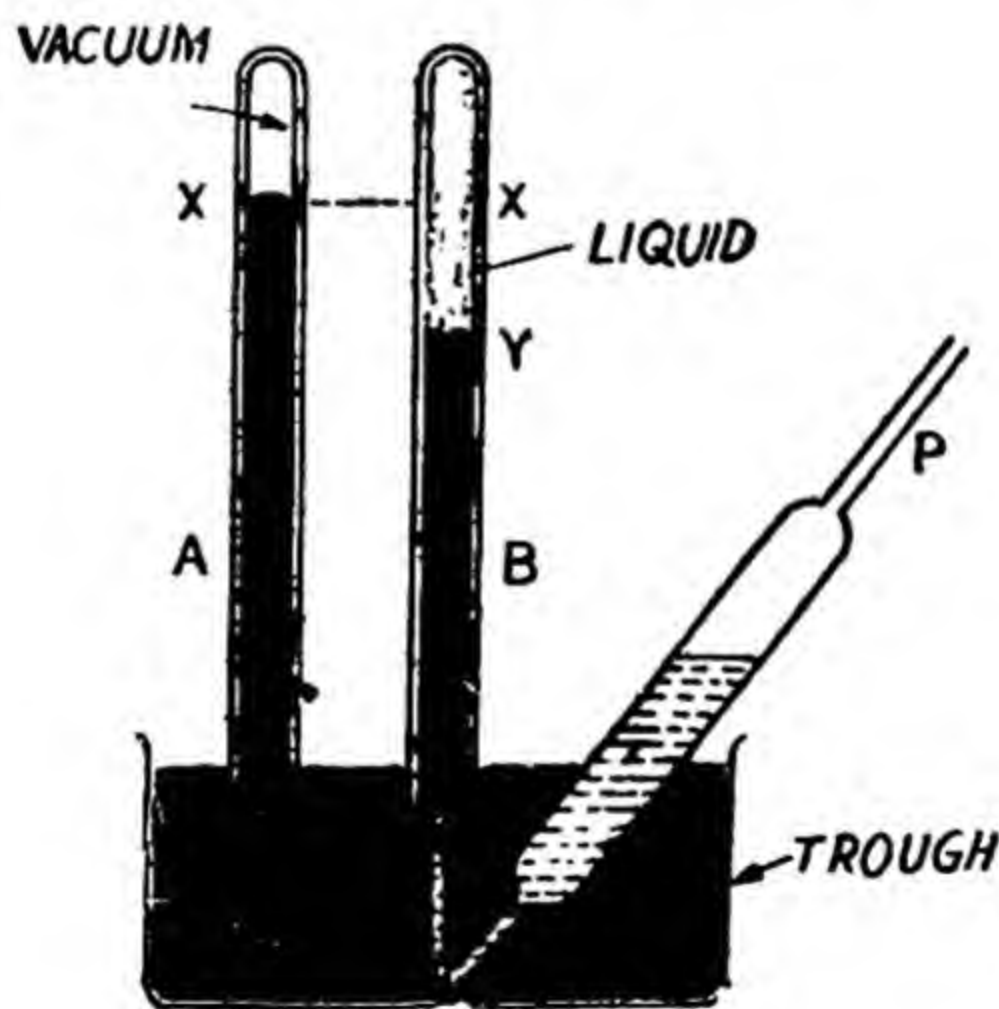


Fig. 9.13

dry mercury and close their open ends with the thumbs and invert them into deep mercury trough as shown in the Fig. 9.13. The mercury in the two tubes will stand at the same level, *X* and *X*. The height of mercury above the mercury surface in the trough indicates the atmospheric pressure. The space above mercury is called the *Torricellian vacuum*.

Let the tube *A* act as a simple barometer tube for comparison. Now introduce a drop of ether into Torricellian vacuum of *B* with the help of a bent pipette, *P*. The ether will at once rise above the surface of mercury in the tube, vaporise and depresses the mercury level in

the tube as shown. This shows that the vapour formed exerts pressure. This pressure is measured by the depression of the mercury column caused by the vapour. Introduce a little more quantity of ether into the tube *B*. It is found that ether again vaporises, but not so quickly as at first, and the column of mercury is further depressed. If the ether is continuously introduced a stage reaches *when it does not vaporise but appears on the surface of the mercury in the form of thin layer of the liquid*. If now more ether is introduced, the mercury column will not be depressed any more. At this stage, the space above the mercury is said to be fully saturated and contains maximum amount of vapour and is not capable of holding any more of the vapour at the given temperature. Thus, *when a space contains the maximum amount of vapour under a given temperature, the vapour is said to be saturated and the pressure it exerts is called the maximum or saturation vapour pressure h* . It is usually referred to as **S.V.P.**

*If the vapour present in the space is less than the maximum that the space can hold at that temperature, the vapour is said to be **unsaturated** vapour. The pressure exerted at this stage is called the **unsaturated vapour pressure**.*

9.19. Properties of saturated vapour. The saturated vapour exerts maximum pressure at a given temperature in a closed space and generally it exists in contact with its own liquid.

- (i) The maximum vapour pressure is different for different liquids.
- (ii) The maximum pressure for the vapour of a liquid at a given temperature is independent of the volume of the space.
- (iii) The maximum vapour pressure depends upon the temperature as shown in the Fig. 9.14. From the figure it is clear that
 - (a) The maximum vapour pressure decreases as the temperature falls.
 - (b) The maximum vapour pressure increases as the temperature rises.

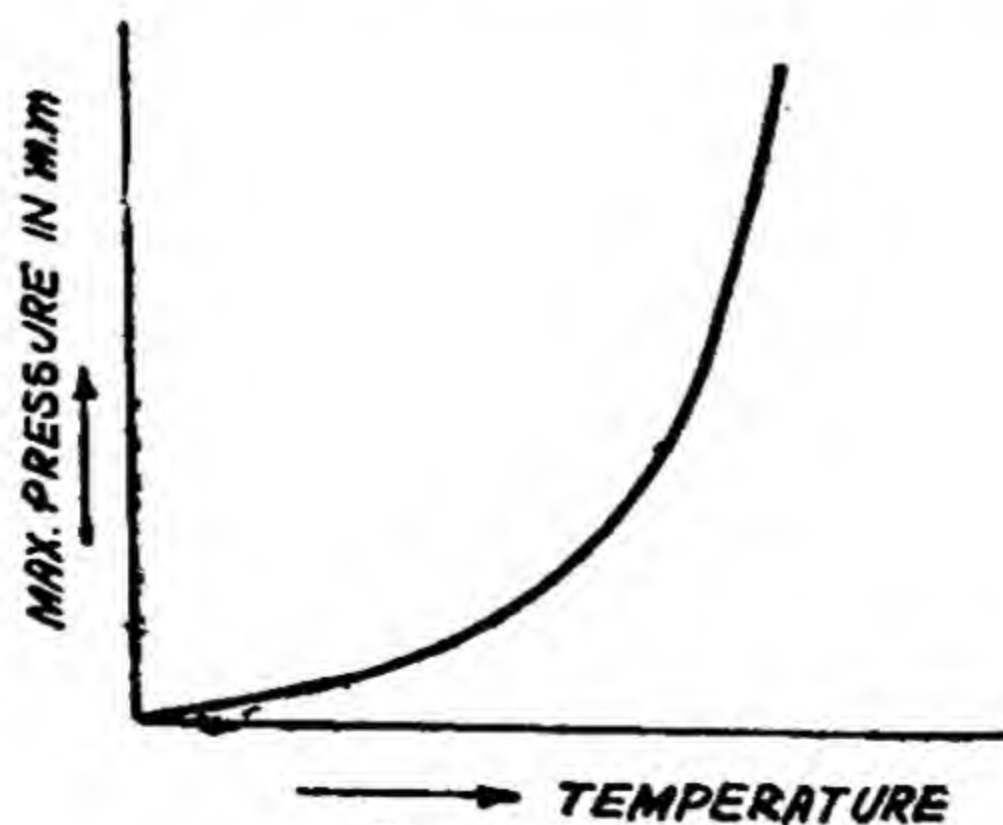


Fig. 9.14.

Note:—The curve is concave upwards the pressure axis which shows that maximum vapour pressure increases rapidly at high temperatures.

9.20. Behaviour of saturated and unsaturated vapours with the change of (a) Volume (b) Temperature.

Consider the vapour of a liquid enclosed in a space above the mercury column in a tube B as shown in Fig. 9.15. To cause a change in the volume of the vapour, the mercury tube can be moved up and down while the change of temperature can be produced by heating or cooling the vapour.

1. Effect of the change of volume on vapour pressure at constant temperature.

Again set two barometer tubes, A and B in a mercury trough as shown in Fig. 9.15. Introduce into B a few drops of water or ether so as to have unsaturated vapour in the space above mercury. The volume of vapour and also the difference between the levels b and c of the mercury column in the two tubes which gives the pressure exerted by the vapour are noted. Now lower B a little into the mercury trough as shown, the volume of the space occupied by the vapour will decrease. As the volume is decreased the mercury column in the tube B is depressed a little more, which shows that the pressure exerted by the vapour has increased. Go on lowering the tube gradually and number of readings for pressures and volume of vapour are taken and it is found that at every stage, the product of pressure and volume remains constant which shows that *an unsaturated vapour behaves like a gas and obeys Boyle's law.*

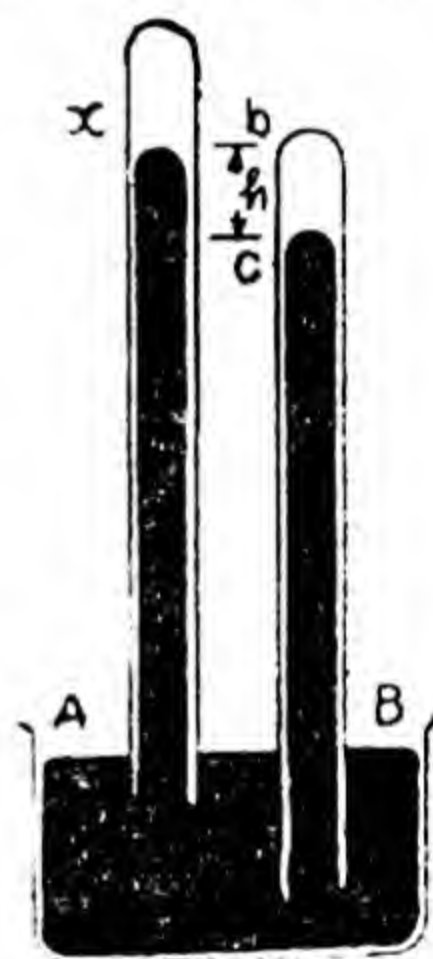


Fig. 9.15

If the volume of the vapour is continuously decreased by pushing the tube down into the trough then a stage is reached when the space above mercury becomes **saturated** with vapour at that temperature. At this stage, the difference h between the levels b and c of mercury in the two tubes gives the maximum vapour pressure at that temperature. Any further lowering of the tube B into the mercury trough does not depress the mercury column any more and thus does not increase the vapour pressure, but simply results in condensation. The volume can now be decreased to any limit without increasing the pressure any further, which shows, **that saturated vapour does not obey Boyle's Law.** Thus it follows that a vapour obeys Boyle's Law so long as it is in its unsaturated stage.

The behaviour of a vapour when its volume is changed at constant temperature is shown in Fig. 9.16. The part AB of the curve indicates that the vapour obeys *Boyle's Law* during its **unsaturated stage**. At the point B corresponding to volume V the vapour becomes saturated and exerts maximum vapour pressure. Any further decrease in volume cause some vapour to condense and the pressure

remains constant. This is shown by horizontal line BC . Thus saturated vapour does not obey Boyle's Law.

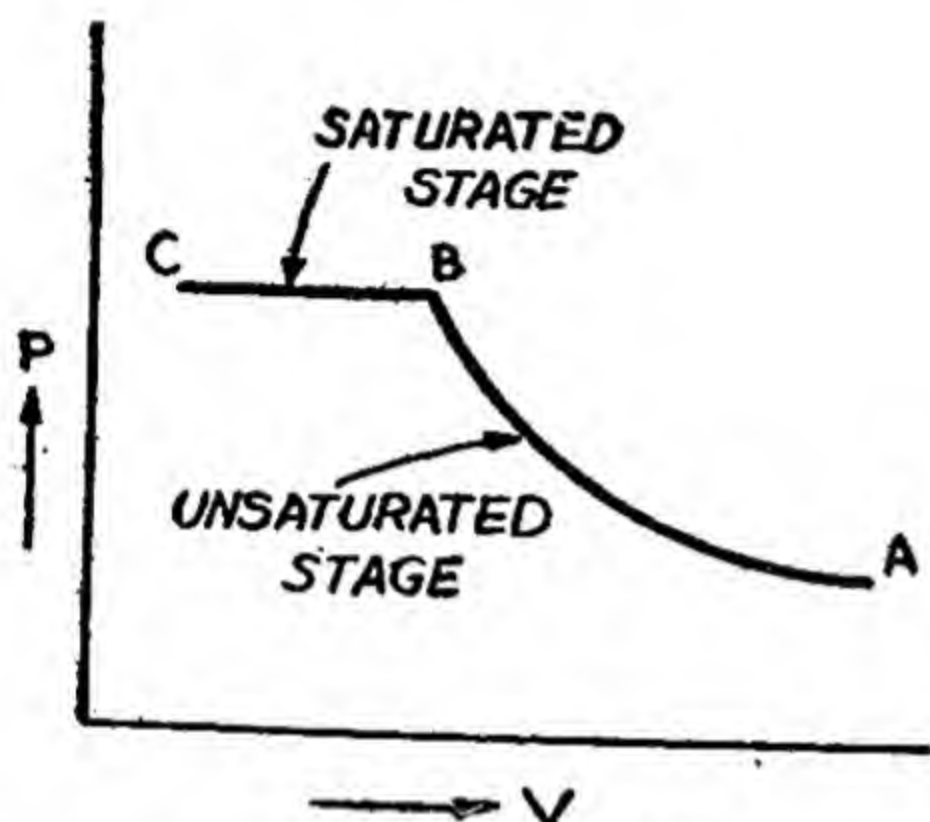


Fig. 9.16.

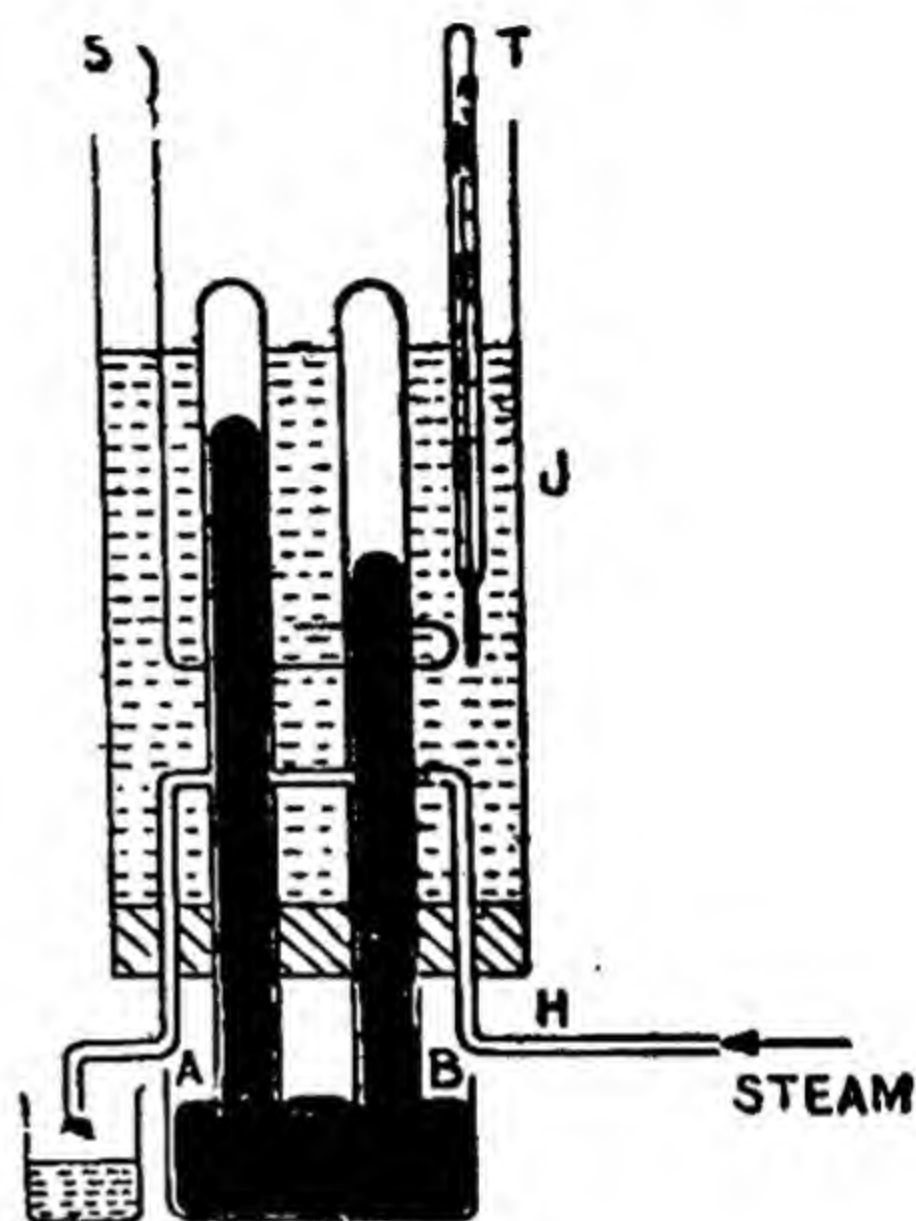


Fig. 9.17.

2. *Effect of temperature on vapour pressure at constant volume.*

Set two barometer tubes A and B and pass them through a cork fitted in the mouth of a wide jacket J as shown in Fig. 9.17. The jacket is filled with water and its temperature can be raised by passing steam through heater tube H immersed in it as shown. The temperature of water can be lowered by adding small pieces of ice in it.

Now raise the temperature of water in the jacket to about 60°C as explained above. Thus insert a few drops of water or ether into the tube B so as to enclose some unsaturated vapour in the space above mercury. The volume and difference in the mercury levels in the two tubes is noted and is the measure of the vapour pressure.

Now lower the temperature of vapour by adding a few pieces of ice in the outer jacket and keep the volume of the vapour constant. A decrease in temperature will increase the height of the mercury column a little which shows that the pressure exerted by the vapour has decreased. If the temperature is further lowered and pressure is measured at different stages then it is seen that when the volume is kept constant the pressure is always proportional to its absolute temperature. *This shows that an unsaturated vapour obeys Charles's Law.*

If the vapour is continued to cool then a temperature is reached when the vapour is able to *saturate* the given space fully and therefore exerts maximum pressure at that temperature. Any further cooling causes the vapour to condense and the vapour pressure will begin to

fall more rapidly with fall in temperature. *This shows that the saturated vapour does not obey Charle's Law.*

The above change in the vapour pressure, when its temperature is varied at constant volume is represented by the curve shown in Fig. 9.18. During the part *AB* of the curve the vapour is in its unsaturated stage and any decrease in temperature produces a proportionate decrease in pressure, so that Charle's Law is being obeyed. When the temperature decreases to *B*, the vapour becomes saturated. Any further decrease in temperature causes some vapours to condense and the pressure begins to fall more rapidly as shown by the curve *BC*. Which shows that it does not obey **Charle's Law.**

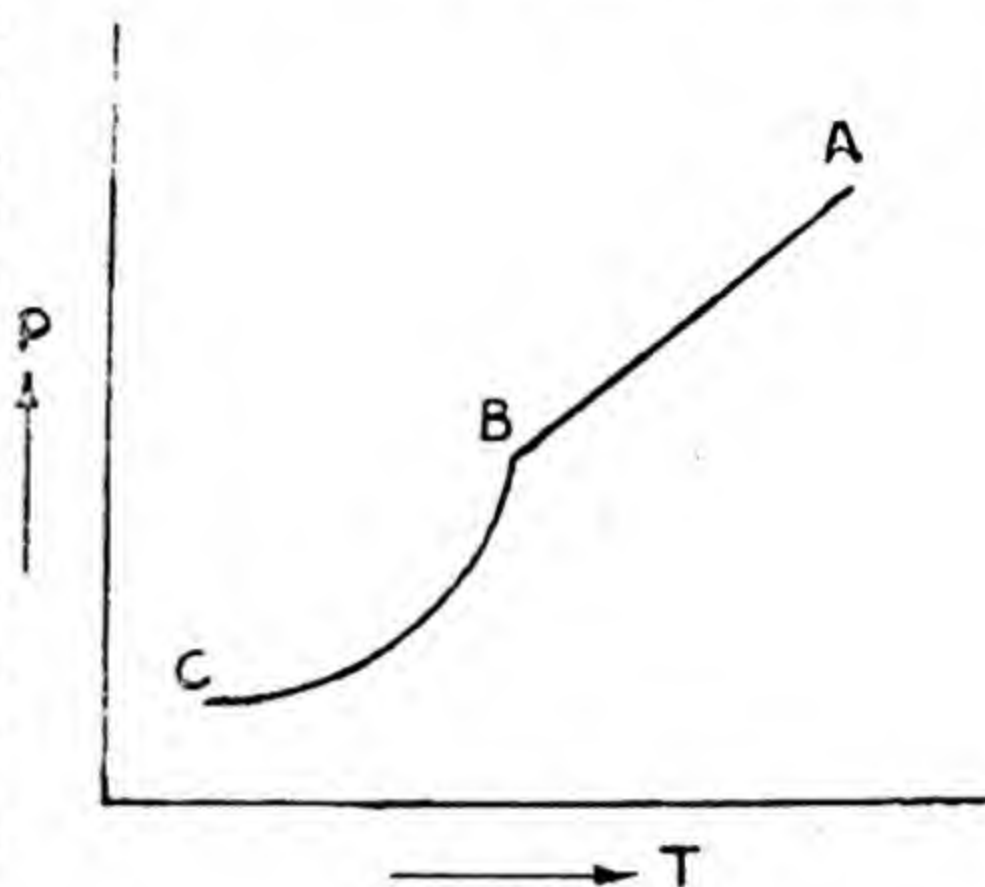


Fig. 9.18.

9.21. Dalton Law of partial pressures. So far we have been dealing with the case of a particular vapour in a closed space. Now we shall study the behaviours of a mixture of vapours and can be stated as follows.

(i) *The saturated vapour pressure in a closed space at a given temperature depends only on the temperature and is independent of the pressure of other vapours or gases having no chemical affinity for each other.*

(ii) *The total pressure exerted in a closed space by a mixture of vapours and gases having no chemical affinity is the sum of the partial pressure which each could exert if it alone occupied the whole space at the same temperature.*

The first law is applicable to saturated vapours and the second law to both saturated and unsaturated vapours.

9.22. Kinetic Theory of Saturation. If at a given temperature a small quantity of liquid is introduced into a closed space at the top of a barometer tube, the whole of the liquid evaporates and the vapour thus formed exerts pressure. To explain this phenomenon on the kinetic theory, let it be assumed that, to start with, more molecules leave the liquid per second, and become gaseous in the closed space, than return to the liquid from the vapour in the closed space. This process continues until no more liquid remains, and unsaturated vapour is obtained.

If now more liquid is introduced into the closed space, a stage is reached when no more of the liquid evaporates and the vapour is now in contact with the liquid. The vapour at this stage is called saturated vapour, at the given temperature. The pressure exerted by this vapour is then maximum and constant at the existing

temperature, no matter how much liquid is introduced into the closed space. This is called the "**saturation vapour pressure**" of the liquid at the given temperature. At this stage the density of the vapour is increased to such a value that the number of molecules leaving the liquid surface per second is the same as the number of molecules returning per-second to the liquid from the vapour. Thus a state of *dynamic equilibrium* exists between the molecules which constitute the vapour and those which constitute the liquid. Further introduction of the liquid into the closed space does not make more molecules to leave the surface per second. It is due to the fact that the speed of the molecules depends only upon the temperature of the liquid. Thus the dynamic equilibrium is maintained with the same average number of molecules of vapour above the surface of the liquid. Therefore this vapour reaches the maximum possible density at the given temperature and is *saturated*. It exerts the maximum possible pressure, known as *saturation vapour pressure*. On decreasing the volume of the space above the liquid more molecules of vapour return to the liquid per second than in the previous case. But the number of molecules leaving the liquid per second remains the same and as a result some quantity of vapour condenses until dynamic equilibrium is again restored. In case the volume of the space above the liquid is increased, the density of the vapour decreases and thus it becomes unsaturated. The density of the vapour again reaches its maximum value by the evaporation of some more liquid and dynamic equilibrium is once again attained. Thus at a given temperature of the liquid, the saturation vapour pressure remains constant.

According to kinetic theory of matter, the molecules of a liquid are in a state of continuous motion. On heating the liquid the mean velocity of the molecules increases, which, therefore run about more rapidly within the liquid. At certain temperature some of the molecules attain so much kinetic energy that they leave the surface of the liquid against the attractive pull of the liquid molecules. It is these escaped molecules which constitute the vapour of the liquid above the surface. Further increase in temperature of the liquid increases the number of molecules leaving the surface per-second. The vapour molecules in motion, in the free space constantly collide with each other and undergo changes in their velocities and directions. These molecules exert pressure when they strike the walls of the container or the liquid surface. The vapour molecules which strike the liquid surface do not get reflected back but are absorbed. On further heating the liquid the number of molecules leaving and returning to the liquid surface increases but is not the same. In a closed space a stage is soon reached when this space cannot accommodate any more vapour molecules. At this temperature, the number of vapour molecules returning to the liquid becomes just equal to the number leaving the liquid surface and dynamic equilibrium is established between the liquid and its vapour. The vapour above the liquid is called saturated at that temperature and the pressure exerted by the

vapour is maximum. This maximum pressure is called saturation vapour pressure.

9.23. Moisture in the air. Evaporation of water continuously takes place at all temperatures from rivers, lakes, oceans and from other wet bodies exposed to air. Animals and plants also constantly give moisture to the atmosphere. Millions of tons of water are thus drawn into the atmosphere every hour. As a result of this the atmosphere always contains some water vapour. Sometimes it contains only a little moisture and has the capacity of absorbing much more of it. At other times, it contains a considerable amount of moisture and can absorb very little or no more. A knowledge of the amount of water vapour or moisture present in air is necessary for the purpose of fore-casting weather or for air conditioning.

The branch of Physics which deals with studying and measuring the amount of water vapours (dampness) in atmosphere is called **Hygrometry**.

Humidity of air. Presence of water vapour in the air is the cause of humidity of air. It may be measured in absolute or relative terms and in the two cases it is respectively known as

(i) Absolute humidity (ii) Relative humidity.

(i) **Absolute humidity.** Dryness or dampness of air is not only determined by the amount of water vapour actually present in certain volume of air but it also depends upon the amount of water vapours required to saturate the same volume of air at the same temperature.

Let 20 gm. of water vapours be contained in one cubic metre of air at 25°C , when 22.5 gm. of water vapours are required to saturate air at that temperature and let 17 gms. of water vapours present in the same volume of air at 20°C when 17.1 gms of water vapours are required to saturate the same volume of air at the same temperature. In the second case though amount of water vapours present in the same volume of air is less yet water vapours are nearly saturated because less amount of water vapours are required to saturate air at 20°C .

Absolute humidity is defined as the amount of water vapours actually present in one cubic metre of air. Its units are gm/cubic metre.

(ii) **Relative humidity.** To get a correct idea of the degree of saturation of air, we must know not only the amount of water vapour actually present in air, but also the amount of vapours required to saturate the same volume at the same temperature. The ratio of these quantities is called the *relative humidity* or simply the *humidity*.

Relative humidity is defined as the ratio of the mass of water vapour actually present in a certain volume of air, to the mass of water vapour required to saturate the same volume of air at the same temperature.

If m is the mass of water vapour actually present in a certain volume of air and M the mass required to saturate the same volume at the same temperature, then

$$\text{Relative humidity, } R.H. = \frac{m}{M}$$

As water vapour obeys Boyle's law up to the saturation stage the density of vapour and hence its mass is proportional to the pressure exerted by it. Thus, the above definition of relative humidity reduces to

$$\text{Relative humidity } R.H. = \frac{p}{P}$$

where p is the actual vapour pressure and P the saturation vapour pressure at the room temperature.

The relative humidity is expressed as a fraction or as a percentage.

Since the saturation vapour pressure decreases as the temperature falls, it is clear that the relative humidity may increase as the temperature falls, or decreases as the temperature rises, without any change in the density of water vapour present.

Dew point. The moisture which is present in air is generally not enough to saturate and the pressure actually exerted by the water vapour is less than the saturation vapour pressure for that temperature. When the air is gradually cooled, a certain lower temperature is reached at which the actual amount of water vapour contained in that portion of the air is just able to saturate it. A slight further cooling will cause the extra vapour (which the air is not capable of holding) to get condensed into water. This temperature at which the condensation just begins is called the **dew point** and it may be defined as follows.

Dew point is that temperature at which the actual mass of water vapour present in a certain volume of air is just able to saturate it.

It is clear from the above that the saturated vapour pressure at dew point is equal to the pressure of the water vapour actually present at the room temperature. Hence the **relative humidity** may also be defined as follows,

$$R.H. = \frac{\text{Saturation vapour pressure at dew point.}}{\text{Saturation vapour pressure at room temperature}}$$

9.24. Mist, Fog and Clouds. When a large volume of air in the unsaturated stage cools down gradually, a stage is reached in which whole of it becomes saturated. The water vapours then condense on small dust particles and we get something known as **mist**. A very dense

mist is ordinarily called **fog**. Fog is generally formed when a mass of warm air becomes sufficiently cooled by coming in contact with the cooled surface of the earth during the evening, night or morning. In autumn or winter, fog is often seen on the water surfaces also.

The mist or fog formed high up in the air is called **cloud**.

Moist air is lighter than dry air. When air after absorbing moisture from the sea surface rises up in the atmosphere it becomes cooled due to following reasons.

(i) the moist air on rising comes in contact with cooler air in the higher regions of atmosphere.

(ii) The expansion of air as it moves up into regions of lower pressure causes cooling.

When the temperature of the ascending air as a whole falls below the dew point the excess of water vapour immediately condenses on floating dust particle as well as on the salt particles coming from the sea along with the air, thus forming a cloud.

Example 5. On a certain day the dew point is 8.5°C and temperature of air is 18.4°C . Find the relative humidity. The maximum vapour pressure at 8°C , 9°C , 18°C and 19°C are respectively 8.04, 8.61, 15.46 and 16.46 m.m. of mercury.

Dew point $= 8.5^{\circ}\text{C}$

max. vapour pressure at $8^{\circ}\text{C} = 8.04 \text{ mm}$

max. vapour pressure at $9^{\circ}\text{C} = 8.61 \text{ mm}$

Increase in vapour pressure for 1°C when temperature increases from 8° to $9^{\circ}\text{C} = 8.61 - 8.04 = 0.57 \text{ mm}$

Increase in vapour pressure for 0.5°C
 $= 0.57 \times 0.5 = 0.285 \text{ mm.}$

Max. vapour pressure at $8.5^{\circ}\text{C} = 8.04 + 0.285 = 8.325 \text{ mm.}$

Temperature of air $= 18.4^{\circ}\text{C}$

Max. vapour pressure at $18^{\circ}\text{C} = 15.46 \text{ mm.}$

Max. vapour pressure at $19^{\circ}\text{C} = 16.46 \text{ mm.}$

Increase in vapour pressure for 1°C when temperature increases from 18°C to $19^{\circ}\text{C} = 16.46 - 15.46 = 1 \text{ mm}$

Increase in vapour pressure for $0.4^{\circ}\text{C} = 1 \times 0.4 = 0.4 \text{ mm.}$

Max. vapour pressure at $18.4^{\circ}\text{C} = 15.46 + 0.4 = 15.86 \text{ mm.}$

\therefore Relative Humidity

$$= \frac{\text{Maximum vapour pressure at dew point}}{\text{Maximum vapour pressure at the temperature of air}} \times 100\%$$

$$= \frac{\text{Maximum vapour pressure at } 8.5^{\circ}\text{C}}{\text{Maximum vapour pressure at } 18.4^{\circ}\text{C}} \times 100\%$$

$$= \frac{8.325}{15.86} \times 100 = 59.5\%$$

Example 6. 40 litres of air at 18°C are passed through drying tubes and the increase in weight produced is 0.396 gm. Having given that 15.2 gms. of water vapour is required to saturate 1 cubic metre of air at 18°C , determine the relative humidity of air.

Increase in weight $= 0.396 \text{ gm.}$

Volume of air passed through drying tubes
 $= 40 \text{ litres}$

\therefore Amount of water vapour actually present in one litre of air,

$$m = \frac{0.396}{40} = 0.0099 \text{ gm.}$$

Amount of water vapour required to saturate 1 cubic metre of air at the same temperature $= 15.2 \text{ gms.}$

Now 1 Cubic metre $= \frac{100 \times 100 \times 100}{1000} = 1000 \text{ litres}$

Mass of the water vapour required to saturate 1 litre of air at the same temperature, $M = \frac{15.2}{1000} = 0.0152 \text{ gm.}$

$$\begin{aligned} \therefore \text{Relative Humidity} &= \frac{m}{M} \times 100 = \frac{0.0099}{0.0152} \times 100 \\ &= 65.1\% \end{aligned}$$

Example 7. What is the degree of saturation in air at 16°C when condensation of moisture takes place at 10°C ? Pressure of water vapour at $16^{\circ}\text{C} = 13.6 \text{ mm}$ and pressure of water vapour at $10^{\circ}\text{C} = 9.2 \text{ mm}$

Since the condensation always takes place at the dew point

\therefore Dew point $= 10^{\circ}\text{C}$

Max. vapour pressure at dew point $p = 9.2 \text{ mm}$

Room temperature $= 16^{\circ}\text{C}$

Maximum vapour pressure at room temperature $P = 13.6 \text{ mm}$

$$\begin{aligned} \therefore \text{Relative Humidity} &= \frac{p}{P} \times 100 = \frac{9.2}{13.6} \times 100 \\ &= 67.65\% \end{aligned}$$

Example 8. The temperature of dew formation was 4.6°C and the temperature of disappearance was 5.4°C . The temperature of the atmosphere was 20°C . Calculate the dew point and the relative humidity.

Saturation vapour pressure of water at $5^{\circ}\text{C}=6.6 \text{ mm}$ and at $20^{\circ}\text{C}=17.5 \text{ mm}$.

Temperature at which dew forms $=4.6^{\circ}\text{C}$

Temperature at which dew disappears $=5.4^{\circ}\text{C}$

\therefore Dew point $=\frac{4.6+5.4}{2}=5^{\circ}\text{C}$

Saturation vapour at 5°C $=6.5 \text{ m.m.}$

Saturation vapour pressure at 20°C $=17.5 \text{ m.m.}$

\therefore Relative humidity $=\frac{\text{Sat. V.P. at dew point}}{\text{Sat. V.P. at room temp.}} \times 100$
 $=\frac{6.5}{17.5} \times 100 = 37.1\%$

Example 9. The temperature of air in a closed space is obtained to be 15°C and the dew point is 8°C . If the temperature falls to 10°C how (i) the pressure of aqueous vapour in air and (ii) dew point are affected. Given pressure of aqueous vapour at $7^{\circ}\text{C}=7.48 \text{ m.m.}$ and at $8^{\circ}\text{C}=8.2 \text{ m.m.}$

The temperature of air in the closed space is 15°C and the dew point is 8°C , hence the vapour in the closed space is unsaturated which obeys Charles' law.

Now pressure at $15^{\circ}\text{C}=\text{Max. Vapour pressure at dew point } 8^{\circ}\text{C}.$
 $=8.02 \text{ m.m.}$

Let P be the pressure of vapour at 10°C , then according to Charles's Law

$$\frac{P}{273+10} = \frac{8.02}{273+15}$$

$$\therefore P = \frac{8.02 \times 283}{288} = 7.88 \text{ m.m.}$$

Example 10. Calculate what fraction of the mass of the water vapours in air would condense if the temperature of the air falls from 20°C to 5°C and if originally the humidity was 60% (Saturation vapour pressure at $20^{\circ}\text{C}=17.6 \text{ m.m.}$ and at $5^{\circ}\text{C}=6.5 \text{ m.m.}$)

Relative humidity $=60\%$

Let p be the actual vapour pressure at 20°C

Saturation vapour pressure at $20^{\circ}\text{C}=17.6 \text{ m.m.}$

We know $R.H. = \frac{p}{P} \times 100$

or $60 = \frac{p}{17.6} \times 100$

$$\therefore p = 17.6 \times \frac{60}{100} = 10.56 \text{ m.m.}$$

Maximum vapour pressure at $5^{\circ}\text{C} = 6.5 \text{ m.m.}$

The temperature falls from 20°C to 5°C , therefore, the vapour pressure falls from 10.56 m.m. to 6.5 m.m.

\therefore Fall in pressure due to condensation

$$= 10.56 - 6.5 = 4.06 \text{ m.m.}$$

$$\therefore \text{Fraction condensed} = \frac{4.06}{10.56} = 0.384$$

Example 11. Calculate the dew point when the relative humidity of air at 20°C is 52%. Given that saturated vapour pressures of water at 20°C , 10°C and 9°C are 17.5, 9.2 & 8.6 m.m. of mercury respectively.

Relative humidity at $20^{\circ}\text{C} = 52\% = 0.52$

Saturated vapour at 20°C , $P = 17.5 \text{ m.m.}$

Let P be the actual vapour at 20°C .

$$\text{Now } R.H. = \frac{p}{P}$$

$$\therefore p = R.H. \times P = 0.52 \times 17.5 = 9.1 \text{ m.m.}$$

Dew point is that temperature at which actual vapour pressure 9.1 m.m. becomes the saturated vapour pressure.

Now saturation vapour pressure at $9^{\circ}\text{C} = 8.6 \text{ m.m.}$

Saturation vapour pressure at $10^{\circ}\text{C} = 9.2 \text{ m.m.}$

\therefore Difference in pressure of 0.6 m.m. corresponds to difference of 1°C

Required difference of pressure $= 9.2 - 9.1 = 0.1 \text{ m.m.}$

Hence difference of 0.1 m.m. will correspond to a difference of

$$\text{temperature of } = \frac{1}{0.6} \times 0.1 = \frac{1}{6} = 0.166^{\circ}\text{C}$$

$$\therefore \text{Dew point} = 10.0 - 0.166 = 9.834^{\circ}\text{C}$$

Example 12. The relative humidity in a closed room at 15°C is 60%. If the temperature rises to 20°C , what will the relative humidity become? On what assumptions are your calculations based? Saturation vapour pressure of water vapour at $15^{\circ}\text{C} = 12.67 \text{ m.m.}$ of mercury, at $20^{\circ}\text{C} = 17.86 \text{ m.m.}$

$$\text{Now } R.H. = \frac{\text{Actual V.P. at room temp.}}{\text{Sat. V.P. at room temp.}}$$

$$\text{or } 0.6 = \frac{p}{12.67}$$

$$\therefore p = 0.6 \times 12.67 = 7.60 \text{ m.m.}$$

Assuming that the unsaturated vapour obeys Charles' Law, we can calculate the value of actual vapour pressure at 20°C .

Now $p_1 = 7.60 \text{ m.m.}$

$$T_1 = 273 + 15 = 288^\circ K$$

$$T_2 = 273 + 20 = 293^\circ K$$

$$p_2 = ?$$

$$\therefore \frac{p_1}{T_1} = \frac{p_2}{T_2} \text{ or } \frac{p_2}{293} = \frac{7.60}{288}$$

$$\text{or } p_2 = \frac{7.60 \times 293}{288} = 7.734 \text{ m.m.}$$

\therefore Relative humidity at $20^\circ C$

$$= \frac{7.734}{17.36} \times 100 = 45\%$$

Example 13. Find the mass of a litre of moist air at a temperature of $32^\circ C$ and pressure of 758.2 m.m. , the dew point being $15^\circ C$. The saturation pressure of aqueous vapour at $32^\circ C$ is 12.7 m.m. The density of dry air at N.T.P. is 1.293 gm/litre .

Pressure due to water vapours = 12.7 m.m.

\therefore pressure due to dry air alone = $758.2 - 12.7 = 745.5 \text{ m.m.}$

Mass of 1 litre of moist air at $32^\circ C$ and at a pressure of 758.6 m.m. = mass of 1 litre of dry air at $32^\circ C$ and at a pressure of 745.5 m.m. + mass of 1 litre of water vapours at $32^\circ C$ at 12.7 m.m. pressure.

Now volume of 1 litre of dry air at $32^\circ C$ and 745.5 m.m.

$$\text{when reduced to N.T.P.} = 1 \times \frac{273}{(273+32)} \times \frac{745.5}{760} \text{ litre} \\ = 0.877 \text{ litre.}$$

Volume of 1 litre of aqueous vapour at $32^\circ C$ and 12.7 m.m.

$$\text{when reduced to N.T.P.} = 1 \times \frac{273}{(273+32)} \times \frac{12.7}{760} = 0.0149 \text{ litre.}$$

\therefore mass of dry air = $0.877 \times 1.293 = 1.136 \text{ gm.}$ and mass of aqueous vapour contained = $0.0149 \times 1.293 \times 0.622 = 0.1203 \text{ gm.}$

Note. [Assuming that the density of aqueous vapour with respect to air is 0.622 .]

\therefore mass of 1 litre of moist air = $1.136 + 0.1203 = 1.14803 \text{ gm.}$

9.25. Hygrometers. Literally hygrometer means an instrument for measuring moisture, or humidity because hygro means moisture. There are a variety of hygrometers which may be broadly classified as,

(i) Absorption hygrometer such as chemical hygrometer.

(ii) Dew point hygrometer such as Daniell's and Regnault's hygrometer.

(iii) Empirical hygrometer such as wet and dry bulb hygrometer and hair hygrometer.

(i) **Chemical hygrometer.** It is the most direct method of determining the absolute humidity of air. The apparatus consists of two U tubes *A* and *B* containing some hygroscopic substances like phosphorous pentoxide or calcium chloride crystals. The tubes are

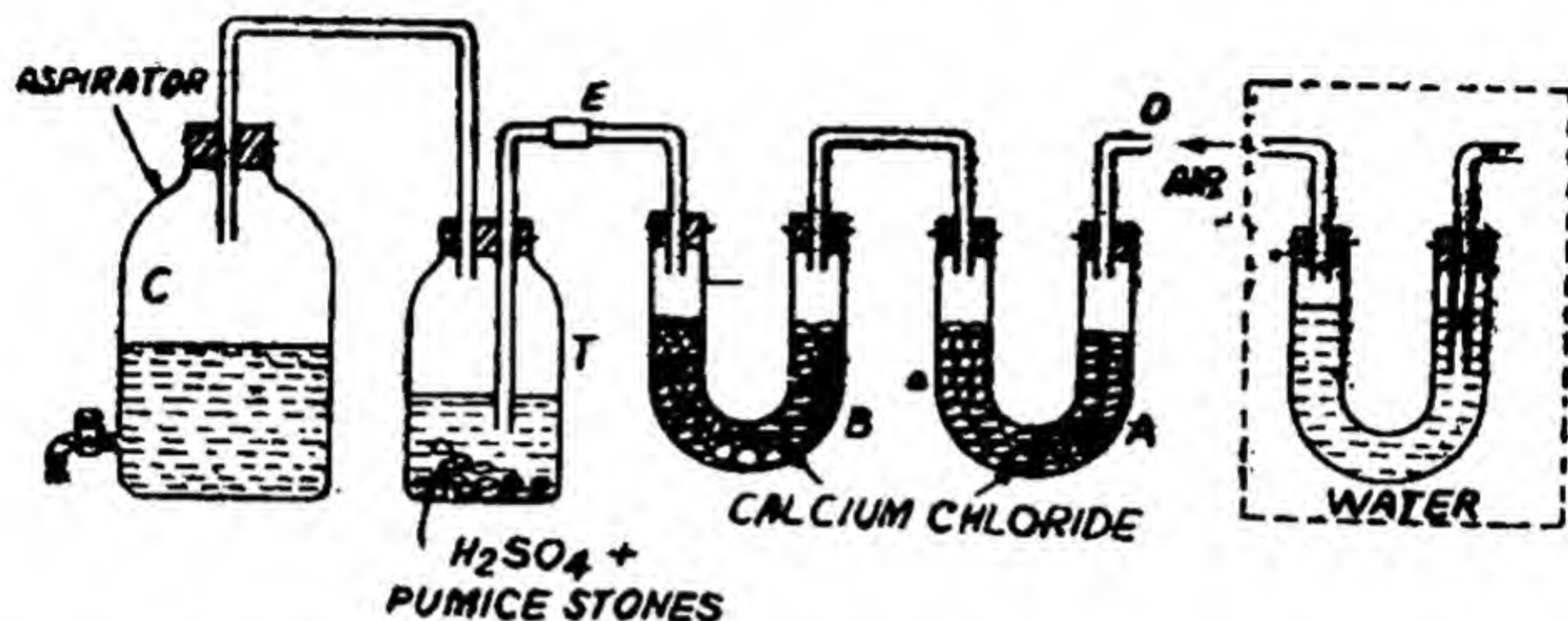


Fig. 9.19

connected by a small rubber tubing *E* to an aspirator *C* through a trap *T*. The trap consists of a bottle containing some pumice stones soaked in sulphuric acid and serves to prevent any moisture from aspirator getting back into the tubes *A* and *B*. The open end of the tube *A* is closed with a plug of cotton.

The aspirator is filled with water and the tubes *A* and *B* are weighed along with their contents before they are put in position. The stop-cock of the aspirator is opened and simultaneously the cotton plug is removed. As the water rushes out of the aspirator the air from the atmosphere is sucked into the U-tubes, its moisture is absorbed by the hygroscopic substance. The water coming out of the aspirator is collected in a measuring cylinder to find out its volume because an equal volume of air enters the aspirator. After about 5 litres of water have flown out the stop cock of the aspirator is closed and at the same time the cotton plug is replaced, the U-tubes are removed and weighed again. The difference in the initial and final readings gives the amount of water vapours present in the volume of air drawn in. Then the **ABSOLUTE HUMIDITY** i.e. the amount of water vapour present in a cubic metre or 10⁶ c.c. of air is calculated.

To find the **relative humidity**, the quantity of water vapours required to saturate that very volume of air at the room temperature is found out from the tables. The ratio of two gives the relative humidity i.e., $\frac{m}{M}$

Where *m*, is the mass of water vapour actually present in a given volume of air at a given temperature.

and M = mass of water vapours required to saturate the same volume of air at the same temperature.

The amount of water vapours required to saturate a cubic metre of air may also be determined experimentally. For this purpose the above experiment is repeated after connecting a U-tube filled with water at D . The air passes through water before entering the tubes containing CaCl_2 and is completely saturated on passing through the U-tube as the whole of the moisture is absorbed. By allowing a certain volume of water to flow out of the aspirator, the quantity of water vapours which saturates one cubic metre of air is calculated.

This method is quite a simple one but it is not so accurate as all water vapours contained in air may not be absorbed. Moreover mass of water vapours absorbed cannot be measured very accurately. Usually, the apparatus is used for standardising other hygrometers.

Example 10. *Two cubic litres of moist air at 30°C were drawn through a chemical hygrometer and 16.8 gm. of water was deposited in the U-tube. Find relative humidity if it is given that at 30°C the mass of water vapours required to saturate one cubic metre of air is 30.1 gm.*

Amount of water vapours in 2 cubic metres = 16.8 gm.

Amount of water vapours in 1 cubic metre $m = \frac{16.8}{2} = 8.4\text{ gm.}$

Also amount of water vapours required to saturate 1 cubic metre of air,
 $M = 30.1\text{ gm.}$

$$\therefore \text{Relative Humidity} = \frac{m}{M} \times 100 = \frac{8.4}{30.1} \times 100 = 27.9\%$$

(ii) **Dew point hygrometers.** These are the instruments which are based upon the determination of **relative humidity** from the knowledge of the dew point. *The dew point is the temperature at which the actual vapour pressure at the room temperature becomes the saturated vapour pressure.*

The principle on which these work is that as the temperature is lowered the surrounding atmosphere approaches the saturation stage till at the dew point condensation starts and the surface of the instrument becomes dim. Thus the relative humidity is calculated by using the relation.

$$R.H. = \frac{\text{Saturation vapour pressure (S.V.P.) at dew point.}}{\text{Saturation vapour pressure (S.V.P.) at room temperature}}$$

There are two kinds of dew point hygrometers which are named as follows :

- (i) Daniel's hygrometer.
- (ii) Regnault's hygrometer.

We shall discuss here only Regnault's hygrometer as it is more accurate.

Regnault's dew point hygrometer. It consists of a wide glass test tube A , the lower portion B of which is replaced by a thin polished silver cap. The mouth of the tube is closed by a cork through which are inserted, a sensitive thermometer T_1 and a bent glass tube G reaching almost to the bottom as shown in Fig. 9.20. A side tube CDE leaves the test tube A near the top and is connected to an aspirator P . A similar tube B is fixed on the same stand and carries a thermometer T_2 . This tube is not connected to the tube A . It is meant for the comparison of the brightness of the polished surfaces of A and B when dew is formed.

To use the instrument the tube A is partly filled with ether so that the lower end of the tube G and the bulb of the thermometer T_1 are well within it. A current of air is drawn through the tube G when the aspirator is worked. The air bubbles out through ether and

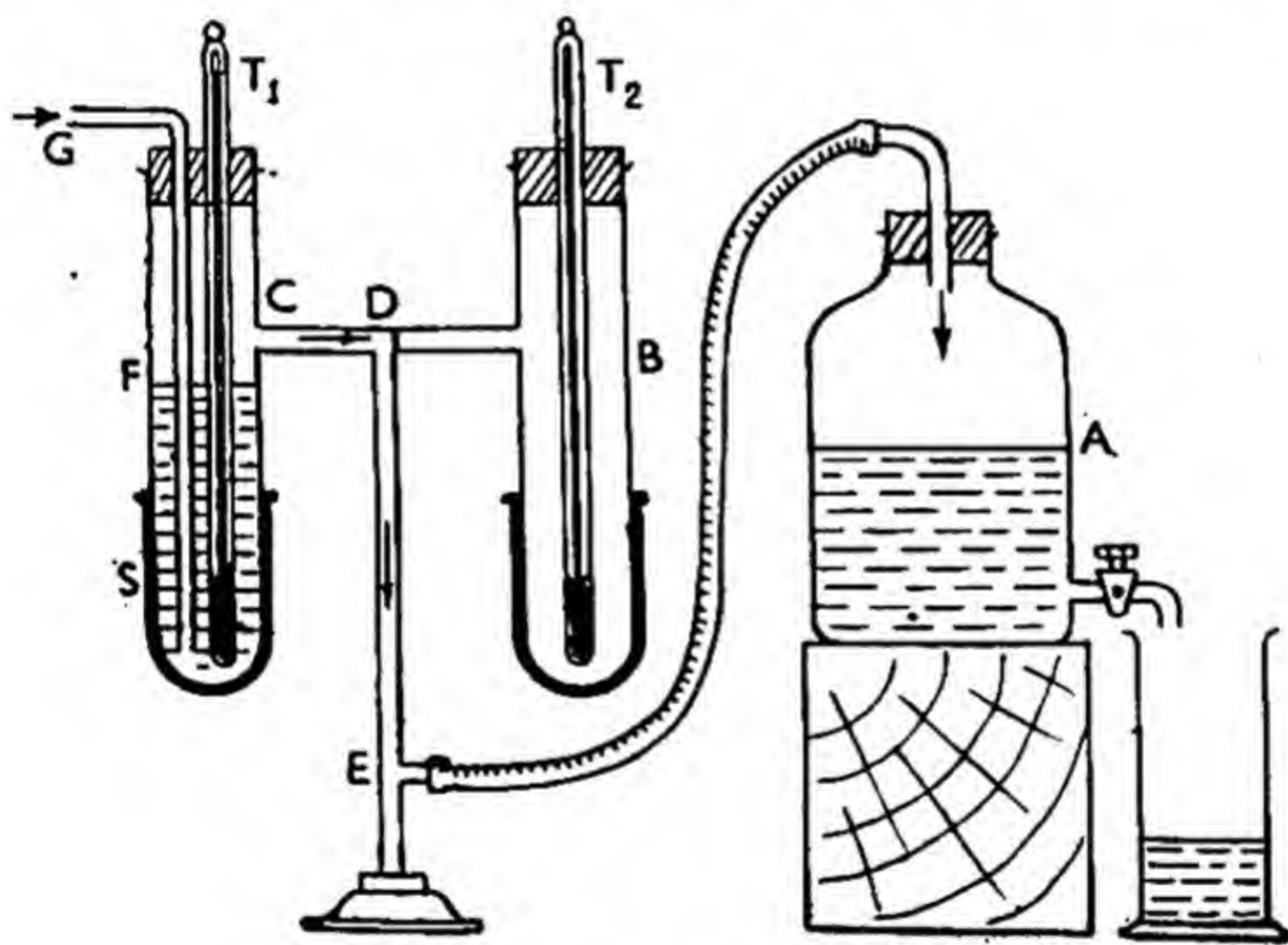


Fig. 9.20

causes it to evaporate. The heat for evaporation is taken from liquid ether thus cooling is caused. As silver is a good conductor of heat it attains the temperature of the liquid ether, both inside and outside. When the temperature of the liquid falls to the dew point a thin film of moisture is condensed on the bright polished surface C of the tube A . This can at once be noted by its comparison with the polished surface of the tube B . The temperature of the thermometer T_1 is noted. The working of the aspirator is stopped and the temperature of the thermometer is again noted when the dew just disappears. The temperature of the room is noted from the thermometer T_2 in the tube B . The mean of the two readings of T_1 gives the dew point.

To find the relative humidity saturated vapour pressure at the dew point and saturated vapour pressure at the room temperature are found.

out from the tables, then

$$R.H. = \frac{\text{Saturated vapour pressure (S.V.P.) at dew point}}{\text{Saturated vapour pressure (S.V.P.) at room temperature}}$$

The advantages of this apparatus are

(i) The rate of cooling can be controlled by adjusting the flow of water from the aspirator.

(ii) The ether is in direct contact with the silver cap so that both are at the same temperature.

(iii) The ether is continuously agitated by the air bubbling throughout its mass.

(iv) The first appearance of dew can be easily detected by comparing the brightness of silver cap *A* with that of *B*.

(v) The observations are taken from a distance with the help of a telescope so that breathing of the observer does not disturb the humidity of air near the apparatus.

(iii) **Wet and Dry Bulb Hygrometer.** This instrument, as shown in Fig. 9 21 is commonly used in meteorological observatory. It depends upon the principle that rate of evaporation depends upon dryness of air. Smaller the humidity greater will be the evaporation and so greater will be the fall of temperature as evaporation causes cooling. It consists of two thermometers fixed on a stand side by side. One of them is simply exposed to the atmosphere and is used for reading temperature of the atmosphere. This thermometer is marked as *D* and is known as dry bulb thermometer. The other thermometer *W* has its bulb wrapped in a piece of wet muslin *M*, which is always kept moist by dipping its free ends into water contained in a small vessel *B*. This is called wet bulb thermometer. Water rises up in the muslin piece by the action of capillarity and evaporates. Due to continuous evaporation of water, cooling is caused as the latent heat involved is being absorbed from the bulb and mercury. This lowers the temperature of the Wet-bulb-thermometer *W*. The rate of evaporation and hence lowering of the temperature depends upon the state of humidity of air. Greater the relative humidity lesser will be the the evaporation and so lesser will be fall of temperature in thermometer *W* thus resulting in lesser difference of temperature between the two thermometers. When relative humidity is 100% then there will be no evaporation and so no fall of temperature

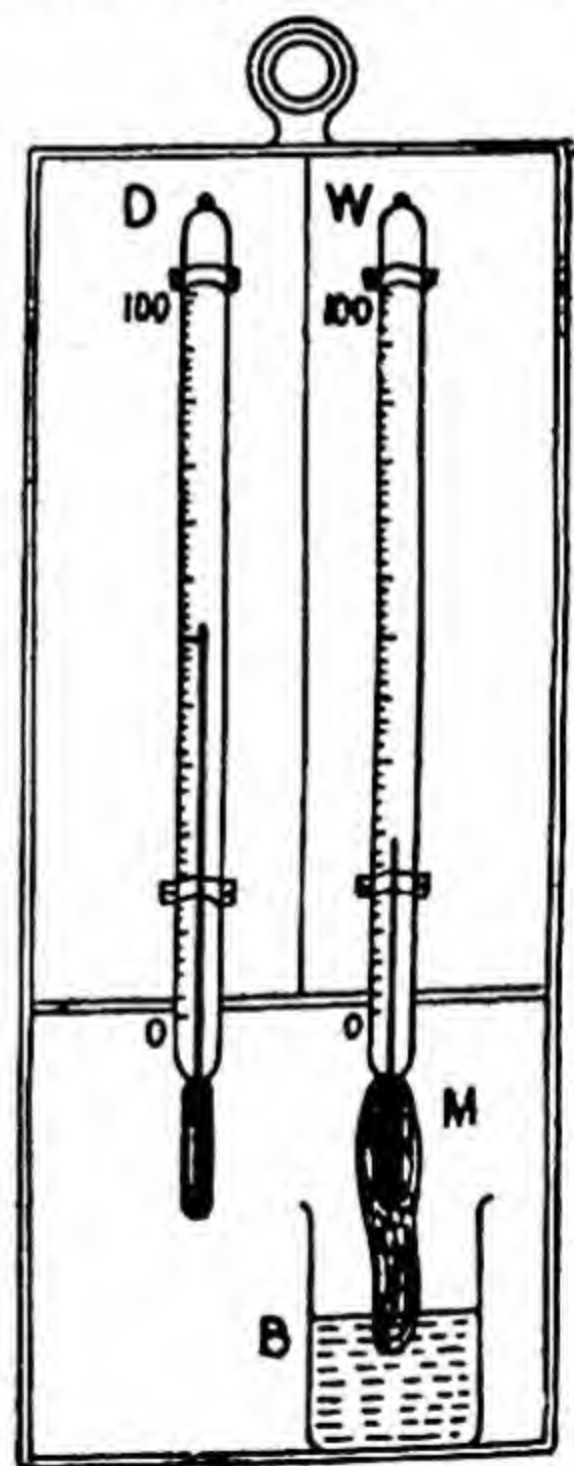


Fig. 9 21

of thermometer W . In this case difference of temperature of two thermometers will be zero. In all other cases temperature of W will always be less than the temperature of D . Hence the difference between the temperatures of the two thermometers is a measure of the $R.H.$ Empirical tables have been prepared from which dew point and relative humidity can be calculated if the lowest wet bulb reading and constant dry bulb readings are known.

(iv) **Hair hygrometer.** It has been found by experiment that human hair expands with increasing relative humidity. One form of hair hygrometer is shown in Fig. 9.22. A long strand of human hair carefully cleaned from all oily matter is fixed at one end A and passes over three small pulleys b, c and d . The hair is then wound a few turns over a revolving small drum e and is finally fastened to the end of a spring s at f . The spring s acting on the drum in the opposite direction keeps the hair taut and the changes in the length of hair cause the movement of the pointer P over a scale which is graduated directly in terms of the relative humidity.

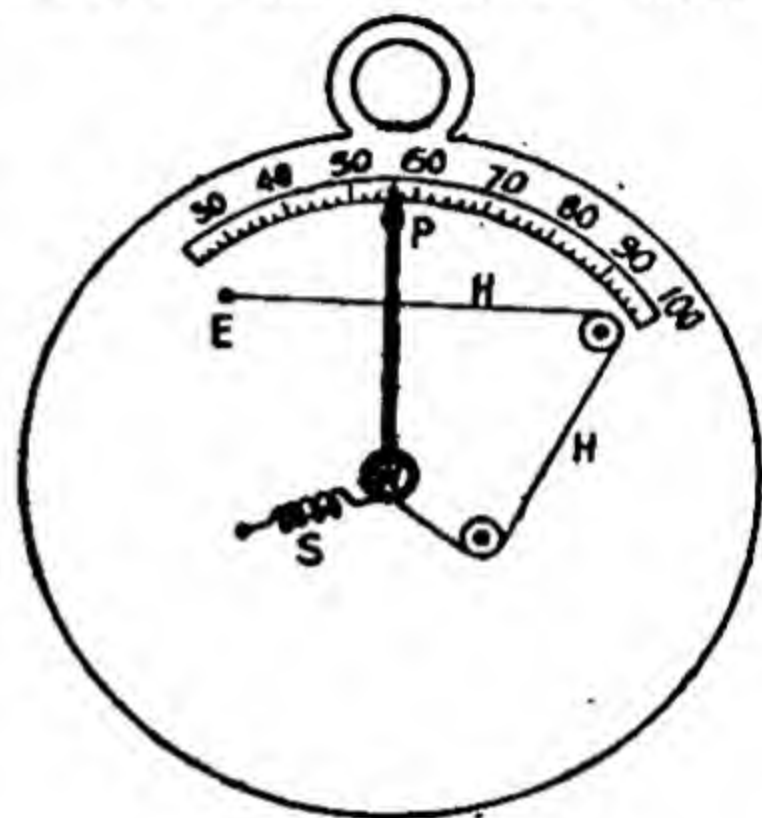


Fig. 9.22

(i) Under normal working conditions, and when subjected to ordinary variations of humidity and temperature, the hair hygrometer tends to give high readings with lapse of time. This is probably due to the fact that the hairs are always under tension and consequently permanent set takes place.

(ii) The most reliable instruments are those in which the tension force is small and the hair is safeguarded from any undue strain.

(iii) The calibration of the instrument should be checked at frequent intervals under normal working conditions.

(iv) It is very important to see that the hair should be free from grease and before it is inserted in the instrument it must be washed in caustic soda otherwise presence of grease will interfere with the absorption of moisture and render the readings of the instrument unreliable.

If suitable precautions are taken the error should not be more than 5 percent. This is usually sufficient for practical working in cold storage and hair hygrometers are often used there. They possess the advantage of being direct reading instruments. Further, they can be employed at a temperature below 0°C where the wet and dry bulb hygrometer present difficulties.

9.26. Importance of Hygrometry. The comfort and the working efficiency of a man is very much affected by the seasonal

variations of temperature, humidity etc. In winter when the temperature is too low, we feel chilly and want to heat our rooms. In summer, we feel hot and wish to cool the rooms. Besides temperature, the humidity of the air also has a great effect on our physical comfort and our health. On a rainy day in summer, we feel far more uncomfortable than on a dry summer day, though the temperature in the later case may be slightly higher. *The reason is that, on a warm rainy day, the humidity of the air is high and the moisture given out by our bodies does not readily evaporate so that we feel uncomfortably damp. But on a fairly dry day even when the temperature is higher, the moisture from our body soon evaporates with consequent cooling, and we feel more at ease.* Similarly, if, in winter the humidity of the air becomes too low, the membranes of our nose and throat are rendered dry and cause considerable discomfort on such a dry day, the skin on the face often cracks producing an itching sensation. Relative humidity of about 50%, is found to be ideal for health. The above facts can be rewritten for complete explanation when the relative humidity rises above 50%, the rate of evaporation from our bodies is very much reduced and we feel oppressive and the rooms appear to be stuffy. When the relative humidity falls below 50% the air becomes dry and evaporation from our bodies is rapid with the result that our throat, nose etc feel dry and thus produce a feeling of irritation.

Hence there is desirability of controlling the humidity in the offices and homes besides the controlling of temperature. In addition to the controlling of temperature and humidity, we also make arrangements for proper circulation of air and to remove dust particles and undesirable odour to make it more comfortable for human beings.

Humidity affects weather, hence regular observations of the changes in the atmospheric humidity help us in predicting the weather which is useful for meteorologists.

The successful working of cold storages for fruit, meat etc often depends upon the degree of control of water vapours present in the enclosure.

The control of humidity is also very important in textile industry specially where cotton and woollen goods are manufactured. Humidity also plays an important role in the artificial seasoning of wood and manufacture of tobacco. It also plays an equally indispensable role in the air-conditioning of building both in summer and winter seasons.

The process of regulating the temperature, humidity, purity and circulation of air is known as Air-conditioning.

EXPECTED QUESTIONS

1. What is meant by 'fusion' and 'point of fusion'? Explain the difference between crystalline and amorphous substances giving a few examples in each case.
2. Explain what is meant by regelation? How will an increase in pressure effect the melting point of (i) ice (ii) wax and (iii) iron? Explain the practical importance of the substances (like antimony etc.) which expand on solidification.

3. How would you define the freezing point of a solution? Is it higher or lower than that of pure solvent? Give a quantitative relation between depression of freezing point and the concentration of the solute. What is molar concentration?

4. Explain fully the following :—

(i) regelation (ii) snow balls (iii) skating.

5. Define the following :—

(i) Le Chatelier's principle

(ii) Eutectic alloy

(iii) Eutectic mixture

(iv) Eutectic proportion

(v) Eutectic temperature.

6. Write short notes on :—

(i) Triple point

(ii) Dew point

(iii) Refrigeration

(iv) Steam line

(v) Hoar frost line

(vi) Ice line

(vii) Sublimation and

(viii) Refrigerant.

7. What is meant by the terms :—

(i) Saturated and

(ii) Unsaturated vapours.

Discuss the relation between :—

(i) pressure and temperature and

(ii) pressure and volume in the case of vapour.

8. What is meant by saturation vapour pressure? What is the effect of compressing

(i) a saturated vapour and

(ii) unsaturated vapour?

9. How is the maximum vapour pressure of a liquid related to its boiling point?

9. Define Relative Humidity and explain how the determination of dew point enables us to calculate the relative humidity at a particular place.

10. A hot day in Calcutta causes more discomfort than an equally hot day in Delhi. Explain it fully.

CHAPTER X

EQUATION OF STATE

10.1. Equation of State. The relation between pressure, volume and temperature of a substance in any state of its aggregation is called the equation of state.

For a perfect gas which obeys both Boyle's and Charles's Laws the equation of a state is expressed as,

$$PV = RT.$$

10.2. Andrew's Experiment. An ideally perfect gas is that which strictly obeys gas laws, *i.e.*, Boyle's Law and Charles' Law. No gas is perfect in the true sense of the word. All gases show some deviation from the gas laws particularly at low temperatures and high pressures. The deviation from the gas laws is also intimately connected with the process of liquifaction of a gas as the deviations are more marked when a gas is nearing liquefaction. To determine the exact conditions required to liquefy a gas Andrews undertook a detailed study of the effect of pressure and temperature on the volume of carbon dioxide.

Andrew's Experiment. Andrews took a glass tube the upper part of which was a graduated capillary tube, the other parts being of wider bore, and passed carbon dioxide through it for 24 hours to remove all traces of air. Both ends were then sealed, and the lower was subsequently reopened under a mercury surface in a container, which could be partially evacuated, so that CO_2 in the tube was adjusted to the required value and trapped by a pellet of mercury. The tube *A* was then mounted with another tube *B* having air above mercury thread, in a vessel consisting of two strong copper cylinders filled with water and having two steel screw plungers *S* and *S'* at the bottom as shown in Fig. 10.1. Both the tubes are connected by a cross tube as shown

Pressures up to 400 atmospheres could thus be produced and communicated to the gas and the air in the two capillaries by comp-

ressing the water by means of either or both screw plungers. Andrews, however never went beyond 108 atmospheres in his own experiment.

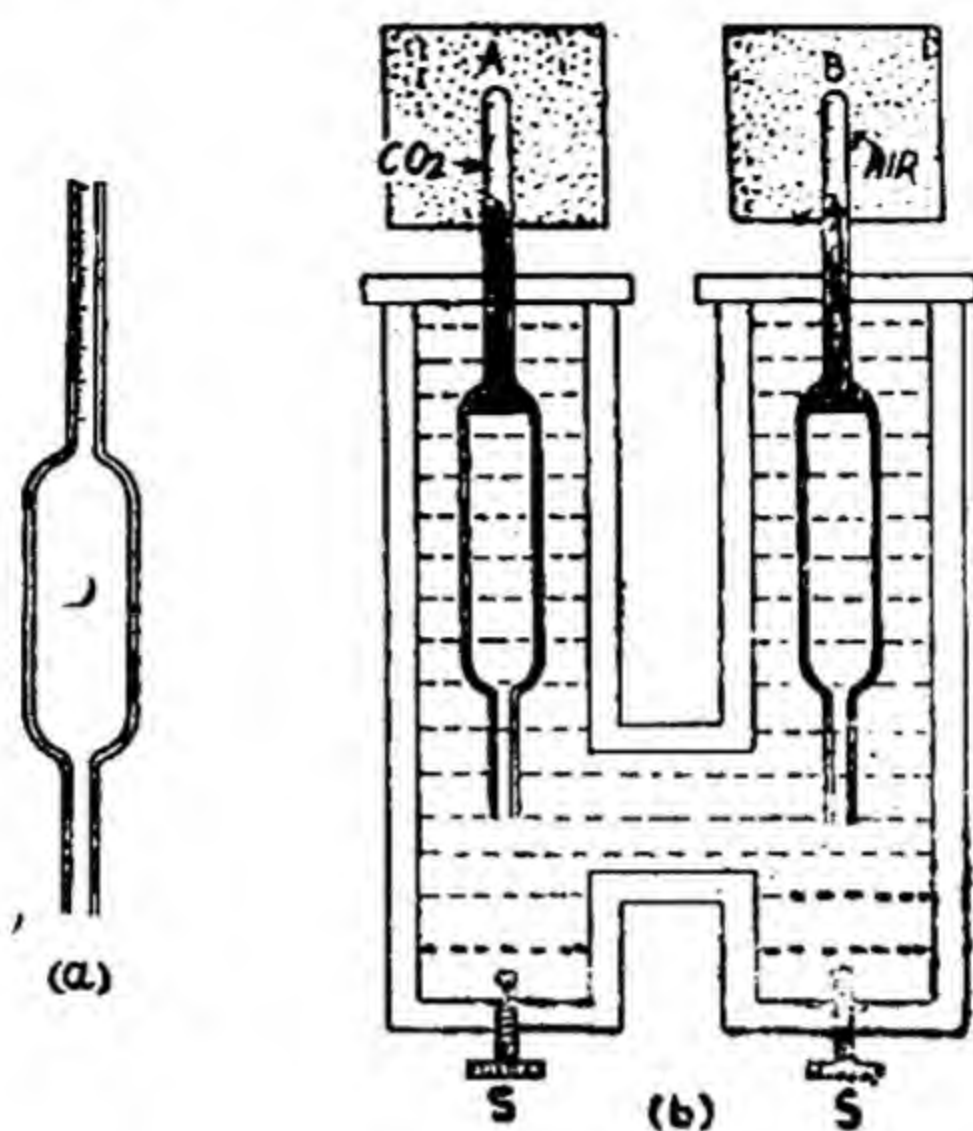


Fig. 10.1

The pressure is determined from the volume occupied by air for which the relation between pressure, volume and temperature is accurately known.

The projecting parts of the capillary tubes were enclosed in two separate water bathes, with one surrounding *A*, maintained at any desired temperature between 0 and 100°C and the other around *B*, at a constant temperature throughout. A number of observations between *P* and *V* at various temperatures are taken and a number of isothermals are drawn.

Note. An isothermal is a curve showing the relation between *P* and *V* at constant temperature.

10.3. General form of isothermals for CO_2 obtained by Andrews. The general form of some of the isothermals obtained for carbon dioxide at different constant temperatures was as shown in Fig. 10.2.

(i) at 13.1°C. Starting with the volume and pressure of the gas, represented by *a* its volume decreases as the pressure increases in approximate obedience to Boyle's Law, where until we reach *b*, where the gas behaves like a saturated vapour and liquefaction commences, with the volume diminishing rapidly and the pressure remaining constant at the value reached at *b*. This progressive liquefaction of the gas continues along the practically horizontal part *b c* of the curve, until at *C*, the whole of it gets liquefied. Any further increase of pressure brings about a negligibly small decrease in volume as the liquids are

almost incompressible. This is shown by the part cd which is a straight line almost parallel to the y -axis.

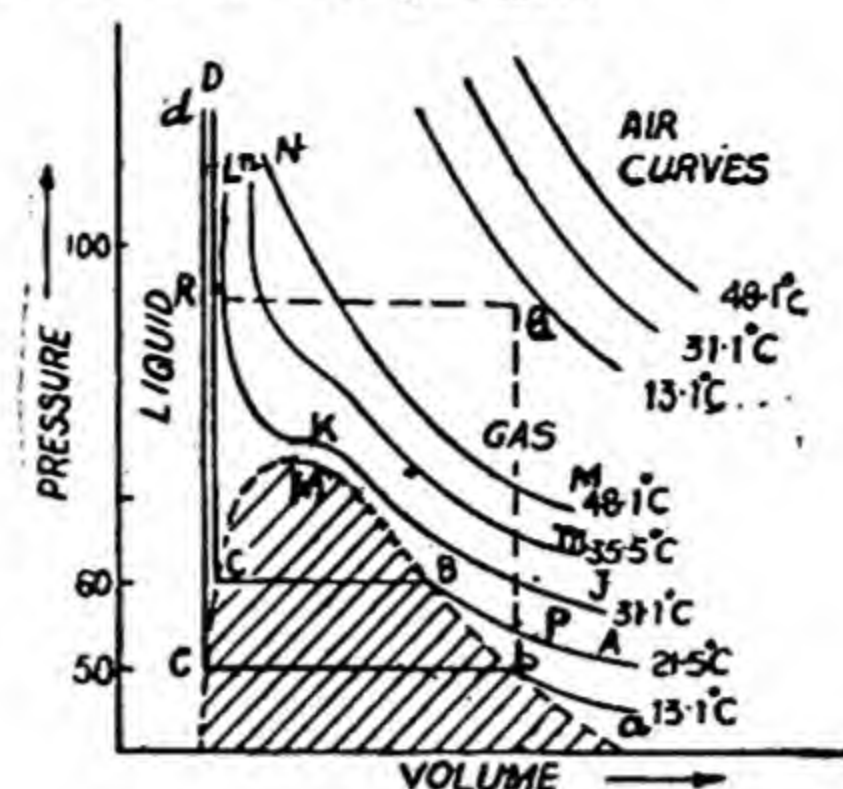


Fig. 10.2

(ii) **at 21.5°C .** The general shape of isothermal for a temperature 21.5°C is again the same. The gas obeys Boyle's law in portion AB which is greater than ab . From B to C the gas behaves as saturated vapour and is in contact with its own liquid. The volume decreases and pressure remains constant. From C to D it is in the liquid state and increase of pressure produces no decrease in volume. The second isothermal differs from the first in the following respects:—

(i) The volume occupied by a given mass of the saturated vapour when condensation starts is smaller; (ii) the volume of the liquid when condensation is complete is larger than that for the first case; and (iii) the horizontal part BC is smaller than the part bc . This shows that with rise of temperature the density of saturated vapour increases and that of the liquid decreases.

(ii) **at 31.1°C .** For the isothermal at 31.1°C , the horizontal portion of the curve has almost disappeared. The curve shows that from J to K and K to L , Boyle's law is obeyed. In fact, the highest temperature at which liquefaction occurs and the isothermal shows a horizontal portion is 30.90°C .

This temperature is known as **critical temperature** and the isothermal corresponding to it is called *critical isothermal*.

(iv) **At temperatures above 31.1°C .** The isotherms for temperatures 35.5°C and 48.1°C much above the critical temperature do not show any horizontal portion and obey Boyle's law from one end to the other. The isothermal for 48.1°C is similar to the isothermal for air shown separately in the same figure.

Discussion. (i) The dotted curve joining the extremities of the horizontal part of these isotherms is called the *border curve*. Its apex M is called the *critical point* and it lies on the critical isothermal. The border curve clearly indicates the different states of a substance. To its right the substance is unsaturated vapour, within it a mixture of saturated vapour and liquid and to its left entirely in the liquid state.

(ii) For every gas there is a *critical temperature* below which a gas must be cooled in order to liquefy it by means of pressure alone. At this temperature the volume and density of the saturated vapour become equal to the volume and density of the liquid. It is not possible to distinguish the vapour (or gas) from the liquid.

The gas behaves almost as a perfect gas above the critical temperature but shows large deviations from Boyle's law at temperatures below the critical value. The pressure necessary to liquefy a gas at the critical temperature is called the **critical pressure** and the volume occupied by a unit mass of the gas at critical temperature is called **critical volume**.

(iii) There exists a continuity of state between the liquid and the gaseous phases. If we start with a given mass of the substance in the state represented by the point *P*, heat it at constant volume until the point *Q* is reached, and then cool it at constant pressure so that the point *R* is reached, then the substance changes from gaseous to liquid form without any discontinuity occurring.

Hence the gaseous and liquid states may be regarded as **distinct stages of a series of continuous physical changes**. In other words a gas and a liquid are widely separated forms of the same condition of matter, which can be made to pass from one to the other by a series of changes so graded that no breach of continuity occurs. Thus at high temperatures and low pressure the substance approximates to the condition of an ideal gas obeying Boyle's law. As the temperature is lowered and the pressure is increased deviation from Boyle's law takes place, the substance slowly acquires the property of a liquid and loses gradually the properties of a gas. At sufficiently low temperature and high pressure the substance entirely becomes a liquid.

✓ 10.4. **Van der Waal's Equation of a Real gas.** No real gas obeys the gas laws perfectly. At ordinary temperatures and pressures the deviation is small but at high pressures and low temperatures the deviations are very large. In the derivation of perfect gas laws on the basis of kinetic theory of gases some assumptions have been made, which do not hold true in the case of real gases. These are

- (i) The molecules are mere mass points having no finite volume.
- (ii) There exists no force of attraction or repulsion between two molecules.

The experiment of Andrews on carbon dioxide and those of Joule—Thomson on the liquefaction of gases have shown that there exists a force of attraction between the molecules of a gas. Though this force of attraction is much less than that in the case of liquids yet it is by no means negligible. Van der Waals therefore rejected the perfect gas equation $PV=RT$, based on the two simplifying assumptions of the kinetic theory, viz., zero size of the molecules and zero force of attraction between them, and presented a modified equation of state for actual gases, taking into account both

molecular size and inter molecular attraction. His equation has not only the merit of simplicity but its general applicability over a wide range of pressures and to larger number of gases.

Correction for the finite size of the molecules. Let $CDEF$ represent a closed space of volume V containing the gas, in which the molecules of the gas are assumed to move. For our present purpose, the molecules are considered as hard elastic spheres with a finite radius. Consider a molecule A moving parallel to CD and suppose it strikes the face of the vessel DE at B and comes back. Now if $CD=l$, the distance travelled by the molecules is not $2l$ but $2(l-d)$ where d is the diameter of the molecule. If we consider the motion of all the molecules in this way, we find that the effective volume in which the molecules move is less than the total volume V of the enclosure. When the pressure is increased, there is a decrease not in the whole volume but a part of it i.e., $(V-b)$ where b is the volume of the portion which can not be compressed. This constant b is four times the total volume of the molecules and not equal to the volume occupied by the molecules, because,

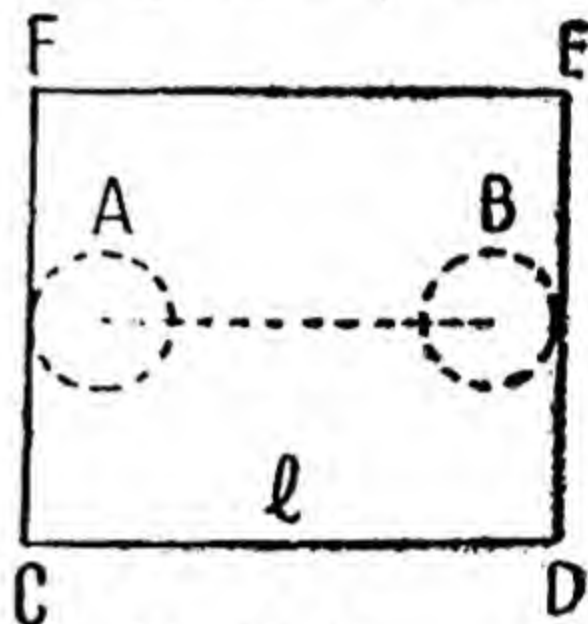


Fig. 19.3.

(a) When all the molecules are moving about, they obstruct each other's motion much more than if some of them were at rest.

(b) Each molecule is surrounded by its sphere of influence the radius of which is greater than the radius of the molecules within which no other molecules can penetrate.

Thus b is the reduction in the effective volume of the gas and is called as *co-volume*. The ideal gas equation, as corrected for molecular size, thus becomes,

$$P(V-b) = RT$$

or

$$P = \frac{RT}{V-b}$$

It is clear from the equation that the effect of the co-volume is to increase the observed pressure.

Correction for inter-molecular attraction. The inter-molecular forces in a gas are probably of the same nature as those which give rise to the phenomenon of surface tension in liquids. The molecules attract one another with a force which varies inversely as some power of the distance between them, so that the attraction is appreciable only for small distances and is negligible for large ones.

Considering a molecule A well inside the vessel it is attracted by other molecules in all directions with the same force and the net force on it is zero. But when it finds itself at a point B near a wall of the vessel, it will experience a pull towards the interior due to unbalanced

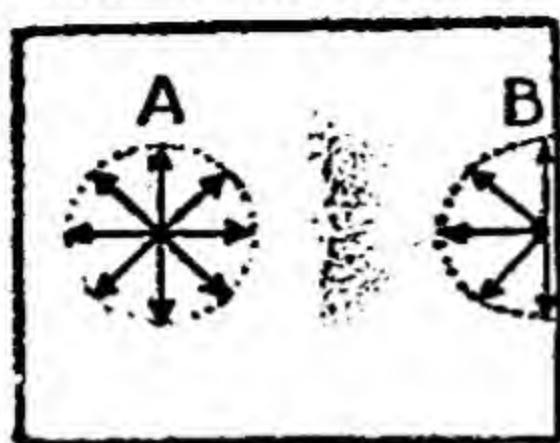


Fig. 10.4.

molecular forces. This pull directed towards the interior and normal to the wall increases from a minimum at a distance equal to the radius of the sphere of influence to a maximum just when the molecule is about to impinge on the wall. Hence the molecule will strike the wall with a velocity less than that with which, it would have struck in the absence of inter-molecular attraction. This is true of every molecule striking the walls of the vessel. The velocity and hence the momentum with which the molecules strike the walls is, therefore, reduced due to the inter-molecular attractions. Naturally when the momentum becomes less the pressure decreases.

The magnitude of this decrease in pressure may be estimated as follows :—

It is due to simple reason that the decrease in pressure is proportional to

- (i) the number of attracting molecules per unit volume, and
- (ii) the number of attracting molecules striking a unit area of the walls of the containing vessel per unit time.

Both these factors are proportional to the number of molecules in unit volume of the gas or to the density of the gas.

$$\therefore \text{Decrease in pressure } p \propto (\text{density of the gas})^2$$

$$\therefore \propto \frac{1}{V^2}$$

$$\text{or } p = \frac{a}{V^2}$$

where a is the constant of proportionality.

Hence the real pressure = Observed pressure + decrease in pressure

$$= P + \frac{a}{V^2}$$

and this value of real pressure should be substituted in the perfect gas equation.

Now, substituting $(V-b)$ for V and $\left(P + \frac{a}{V^2}\right)$ for P , we have

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT$$

This equation is known as Van-der Waal's equation of state.

Comparison with experimental facts, Van-der-Waals' equation is not perfect. It is only reaching perfection. We will test the theoretical results obtained from Van-der-Waals' equation by draw-

ing the isothermals for carbon dioxide and comparing them with the experimental result of Andrews.

The theoretical curves are shown in Fig. 10.5 whereas the experimental curves are given in Fig. 10.2

It is clear that theoretical curves for high temperature agree closely with the experimental ones.

(i) Compare the isothermals for 21.5°C . The part $A'B'$ is similar to the part AB . Similarly the portion $C'D'$ is also similar to the portion CD .

(ii) The portion $B'XYC'$ does not agree with the experimental portion BC , whereas the experimental portion is straight the theoretical curve shows a maximum at X and a minimum at Y .

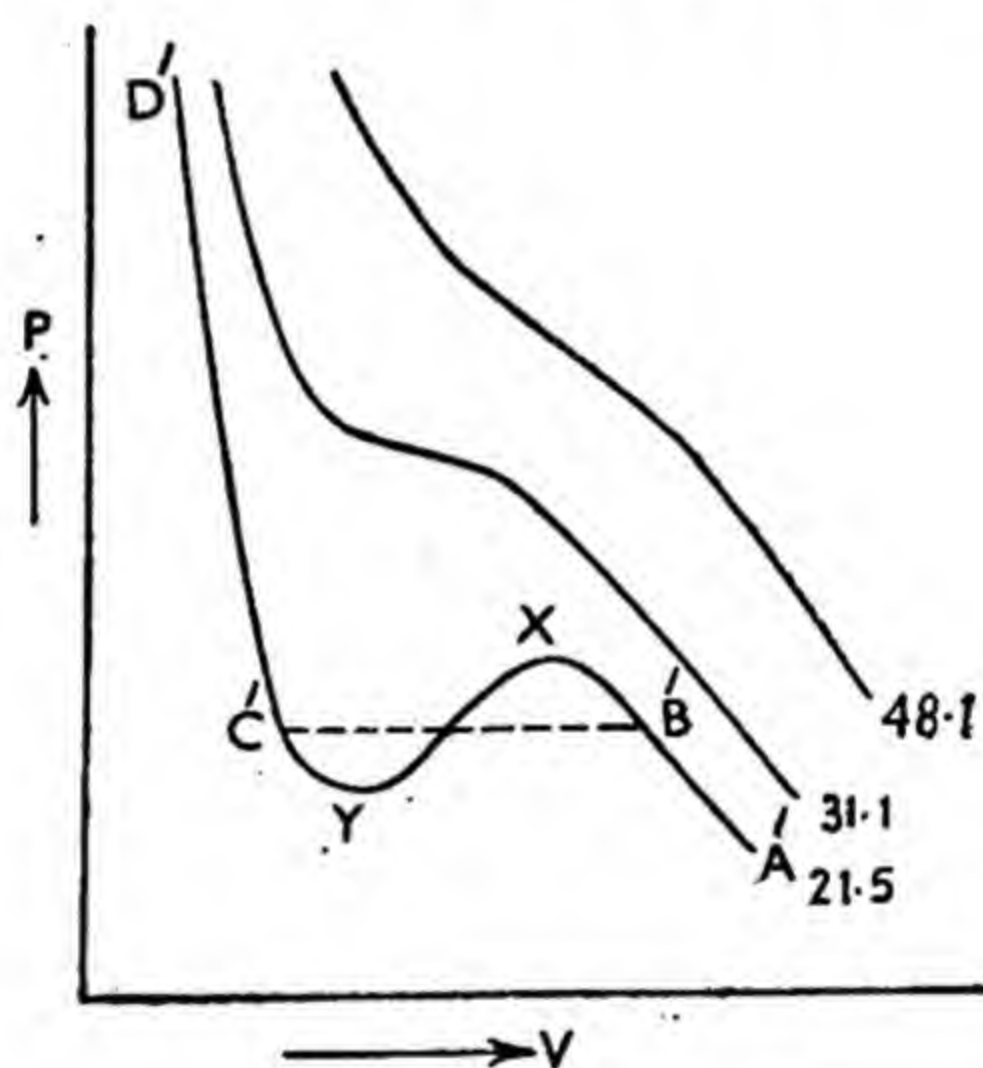


Fig. 10.5

This deviation has been explained by Thomson considering the phenomenon of super-saturation.

If liquefaction had started at B' the portion $B'X$ would have been absent. It, therefore, represents the unstable state of *super-saturated vapour*. It is possible under certain conditions to compress a vapour beyond the saturation stage without liquefying it. The portion $C'Y$ represents the unstable state called the *superheated liquid*. It is sometimes possible to heat a liquid above its boiling point without allowing the liquid to boil and change into vapour form.

The portion XY represents an anomalous behaviour, that the volume decreases as the pressure is decreased. It cannot be realised in practice.

10.5. Van-der Waals equation and critical constants. Van-der Waals equation may be written in the form

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where P , V and T are the pressure, volume and absolute temperature of the gas respectively and a , b and R are constants. On expanding the above equation we get,

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

Multiplying by V^2 , we have

$$PV^3 - PbV^2 + aV - ab = V^2RT$$

Rearranging the terms, we get

$$PV^3 - V^2(Pb + RT) + aV - ab = 0$$

Dividing by P , we get

$$V^3 - V^2\left(b + \frac{RT}{P}\right) + \frac{a}{P} - \frac{ab}{P} = 0 \quad \dots(i)$$

This is a cubic equation in V and has *three* roots i.e., in general, there are three values of V for a given value of P and T . At the critical point all the three roots will be equal since a gas has only one value of volume, pressure and temperature corresponding to it.

Let x be the value of this critical volume, then

$$V = x \text{ or } V - x = 0$$

$$\therefore (V - x)^3 = 0$$

$$\text{or } V^3 - V^2 \cdot 3x + V \cdot 3x^2 - x^3 = 0 \quad \dots(ii)$$

Comparing the co-efficients of V^2 , V , and the constant term in (i) and (ii), we have

$$3x = b + \frac{RT}{P} \quad \dots(iii)$$

$$3x^2 = \frac{a}{P} \quad \dots(iv)$$

$$x^3 = \frac{ab}{P} \quad \dots(v)$$

Dividing (v) by (iv), we get

$$\frac{x}{3} = \frac{ab}{P} \times \frac{P}{a} = b$$

or

$$x = 3b$$

∴ Critical volume $V_c = 3b$

Substituting the value of x in equation (iv), we have

$$3 \times 9b^2 = \frac{a}{P}$$

or

$$P = \frac{a}{27b^2}$$

∴ Critical pressure $P_c = \frac{a}{27b^2}$

Substituting the value of x and P in (iii), we have

$$3 \times 3b = b + \frac{RT}{a} \times 27b^2$$

∴ $8a = 27b RT$

or

$$T = \frac{8a}{27 Rb}$$

∴ Critical temperature

$$T_c = \frac{8a}{27 Rb}$$

Hence

$$P_c = \frac{a}{27 b^2} ; T_c = \frac{8a}{27 Rb} \text{ and } V_c = 3b$$

From the above values, it is seen that

$$\frac{RT_c}{P_c V_c} = \frac{8}{3} = 2.667$$

This ratio is called critical coefficient though its theoretical value is $\frac{8}{3}$, its actual value found experimentally is much more than this for different gases.

Example 1. Calculate the value of critical temperature for CO_2 for which $a = 0.00874$ atmosphere and $b = 0.0023$ c.c.

We know that

$$T_c = \frac{8a}{27Rb}$$

The value, of a and b given are in atmospheres and in c.c. respectively. To find the value of critical temperature let us first

calculate the value of R at a pressure of 1 atmosphere for a volume of 1 c.c. at 0°C or 273°K from Van-der Waal's equation.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

Substituting the values we get,

$$\left(1 + \frac{0.00874}{1^2}\right)(1 - 0.0023) = R \times 273$$

or

$$R = \frac{1.00875 \times 272}{273}$$

Now

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 0.00874 \times 273}{27 \times 1.00874 \times 0.9977 \times 0.0023} = 306^\circ\text{K or } 33^\circ\text{C}$$

10.6. Defects in Van-der Waal's equation.

- (1) It does not tell us when the condensation begins.
- (2) The values of a and b do not remain constant at all temperatures.
- (3) If we calculate the critical constants we find that

$$\frac{RT_c}{P_c V_c} = \frac{8}{3}$$

for all gases but actually volume of $\frac{RT_c}{P_c V_c}$ varies with the gas and has an average value of 3.77.

- (4) Also the critical value $V_c = 3b$ theoretically, though experimentally it is equal to $2b$.

10.7. Reduced equation of state. An equation which expresses the relation between the pressure, volume and temperature of a gas is called the **equation of a state or the characteristic equation**. If we express pressure, volume and temperature of a gas as fractions of their respective critical values and substitute these for P, V and T in Van-der Waal's equation, we obtain a reduced equation of state, which is the same for all gases. This principle is known as the law of *corresponding states* and the equation of state obtained is therefore, *corresponding state equation or the reduced equation of state*.

Thus, putting the pressure P , volume V and temperature T of a gas as fractions of their respective critical values, we have

$$\frac{P}{P_c} = \alpha, \quad \frac{V}{V_c} = \beta \quad \text{and} \quad \frac{T}{T_c} = \gamma,$$

so that $P = \alpha P_c$, $V = \beta V_c$ and $T = \gamma T_c$

where α , β and γ represent fractions and are called reduced (representative) pressure, volume and temperature respectively and are together referred as reduced variables of state.

Substituting the values of P , V and T in the equation

$$\left(P + \frac{a}{V^2} \right) (V - b) = RT, \text{ we get}$$

$$\left(\alpha P_c + \frac{a}{\beta^2 V_c^2} \right) (\beta V_c - b) = R \gamma T_c$$

Now $P_c = \frac{a}{27b^2}$, $V_c = 3b$ and $T_c = \frac{8a}{27Rb}$

$$\therefore \left(\alpha \frac{a}{27b^2} + \frac{a}{\beta^2 9b^2} \right) (\beta \cdot 3b - b) = R \gamma \frac{8a}{27Rb}$$

or $\frac{a}{27b^2} \left(\alpha + \frac{3}{\beta^2} \right) \times 3b \left(\beta - \frac{1}{3} \right) = \frac{a}{9b} \cdot \frac{8\gamma}{3}$

$$\left(\alpha + \frac{3}{\beta^2} \right) \left(\beta - \frac{1}{3} \right) = \frac{8}{3} \gamma.$$

This is the *reduced equation of state*. This equation is independent of any property particular to any gas and is therefore, applicable to all gases. Let two gases have the reduced variables α_1 , β_1 , γ_1 and α_2 , β_2 , γ_2 respectively. Then clearly

$$\left(\alpha_1 + \frac{3}{\beta_1^2} \right) \left(\beta_1 - \frac{1}{3} \right) = \frac{8\gamma_1}{3} \text{ for one gas.}$$

and $\left(\alpha_2 + \frac{3}{\beta_2^2} \right) \left(\beta_2 - \frac{1}{3} \right) = \frac{8\gamma_2}{3} \text{ for the other gas}$

Obviously therefore if $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2$ we shall have $\gamma_1 = \gamma_2$.

10.8. Liquefaction of gases. It was observed that substances which were gaseous at ordinary temperature could be converted into a liquid state if sufficiently cooled and simultaneously subjected to a high pressure. Faraday in 1823 was able to liquefy chlorine and other similar gases. During the succeeding years, other gases like CO_2 , hydrogen sulphide, nitrous oxide and hydrogen chloride were liquefied under compression with the aid of simple freezing mixture.

In general there are two methods by which gases may be liquefied. The first method has been mentioned above. The second method consists of cooling the gas below its critical temperature and then applying a sufficiently high pressure.

The three main methods by which gases can be cooled are :—

1. **Cascade process**, which utilizes a series of liquids with successively lower boiling points to reach the low temperature in stages.

2. **Regenerative Joule—Thomson, process**, based on the Joule-Thomson effect and regenerative cooling.

3. **Adiabatic expansion process**, based on the cooling produced when a gas expands adiabatically doing external work.

1. **The Pictet or Cascade process for liquefying oxygen.** If we wish to liquefy oxygen, we must in some way cool the gas below its critical temperature apart from any increase in pressure. In 1878 Pictet working independently brought about the liquefaction of oxygen. Pictet made use of the cooling effect of a liquid which was rapidly evaporated. His method is often known as, **Cascade Process** and it may be described as a number of compression machines in series, each machine reducing the temperature of the liquid to a lower value than its predecessor. First of all a gas like methyl chloride (CH_3Cl) is liquefied and then allowed to evaporate under reduced pressure. The cooling so produced is utilised in reducing the temperature of ethylene (C_2H_4) by passing it through a spiral coil immersed in liquid.

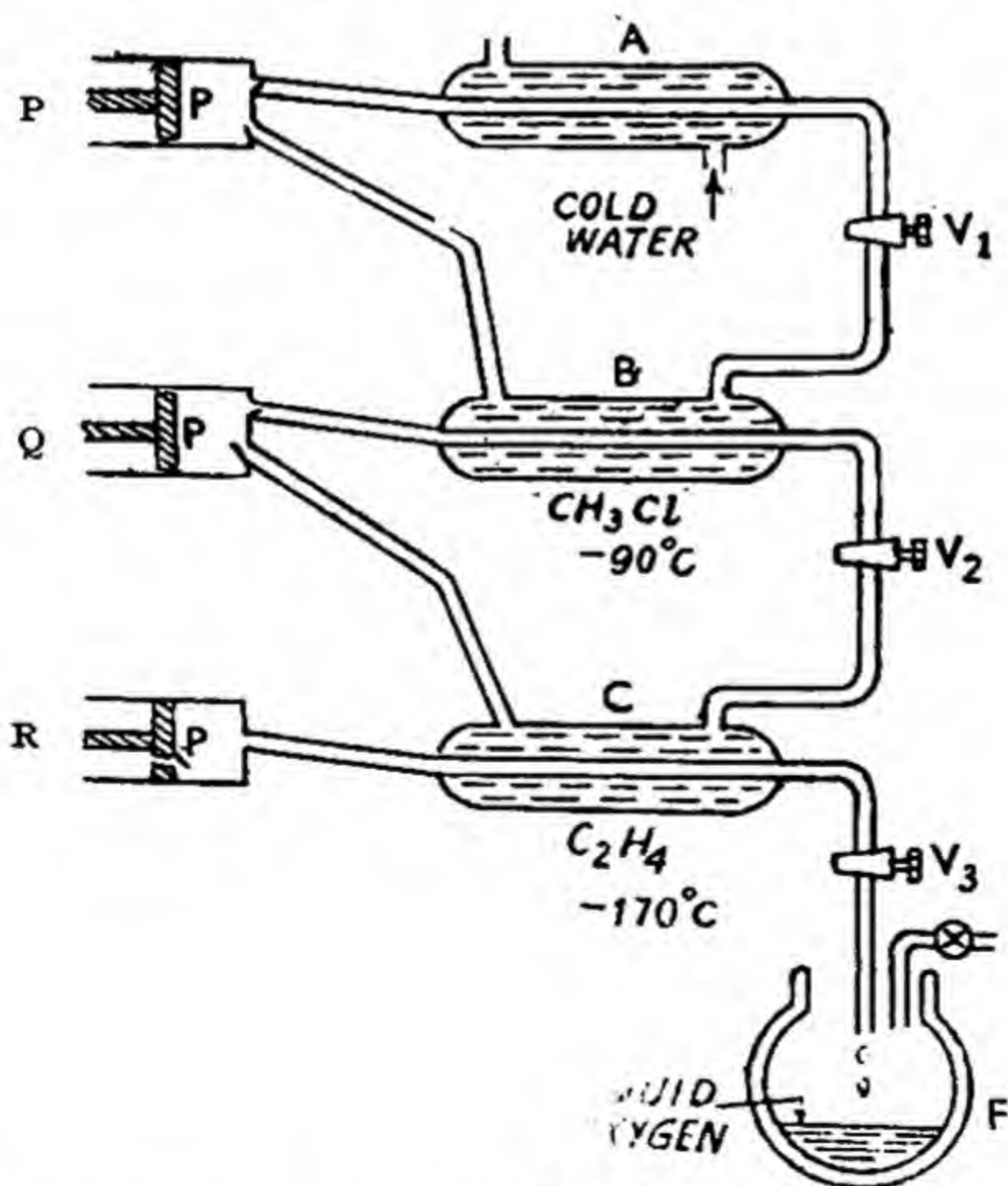


Fig. 10.6

methyl-chloride. When ethylene liquefies, it is also allowed to evaporate under reduced pressure till its temperature falls below the critical temperature of oxygen. Then oxygen under high pressure is

passed through ethylene. Oxygen liquefies at a pressure of about 20 atmospheres, when its temperature falls below -118°C . Oxygen therefore, must be cooled to a temperature below this particular temperature if it is to be liquefied. About the same time, **Kamer leigh Onnes** also employed the cascade process for liquefaction of oxygen, using methyl chloride and ethylene for his two working substances. His apparatus is shown diagrammatically in Fig. 10.6

It consists of three compressor machines *A*, *B* and *C* working in series by means of three pumps *P*, *Q* and *R*. Machine *A* is filled with methyl chloride and surrounded by cold water. Since critical temperature of methyl chloride is 143°C , it can be liquefied at the room temperature with a pressure of few atmospheres.

Compressed methyl chloride gas from pump *P* is passed through the spiral tube (shown straight in the figure), inside the compressor machine *A*, while cold water is circulated through the inner jacket of *A*. Liquid methyl chloride thus obtained is made to circulate the jacket of the compressor machine *B* of the second unit, which is connected to the suction side of *P*. This enables the liquid methyl chloride, which normally boils at -24°C , to evaporate under reduced pressure and produce a fall of temperature to about -90°C in *B*. Compressed Ethylene from pump *Q* is passed through the spiral tube inside the compressor machine *B*. Since it has a critical temperature of 9.5°C , it is readily liquefied in *B* maintained at about -90°C by the continuous circulation of liquid methyl chloride through it. Liquid ethylene formed in *B* is made to flow round the jacket of the compressor machine *C* of the third unit and at the same time allowed to evaporate under reduced pressure by connecting the jacket of *C* to the suction side of *Q*. The temperature of compressor machine *C* thereby falls to about -160°C , although the boiling point of ethylene is 104°C . Compressed oxygen from the pump *R* passes through the spiral tube inside *C* where it is easily liquefied since its critical temperature is only -118°C . Liquid oxygen is collected in a Dewar flask *F*. The lowest temperature attained by boiling liquid oxygen under reduced pressure is -218°C .

This method may be continued in order to liquefy nitrogen or neon, but fails when applied to hydrogen or helium, because it is not possible in this way to reach a temperature below the critical temperature for these gases.

2. Liquefaction of air (Linde's method) This is based upon Joule-Kelvin (Thomson) effect.

Joule performed experiments to find cooling produced when compressed air in one vessel was allowed to expand into an other evacuated vessel, through a narrow orifice. These experiments indicated that in the whole no change of temperature was observed. His experiments were incapable of giving accurate results as the heat capacity of the gas was small as compared to the heat capacity of the calorimeter used by him.

Joule and Lord Kelvin (Thomson) later performed more accurate experiments and found that the cooling effect was observed in all gases except hydrogen. **The cooling produced when a gas is allowed to expand through a narrow orifice is called Joule-Kelvin effect** and it was proved by this principle that a gas is cooled when forced through a narrow orifice provided the temperature at which the process takes place is below the temperature of inversion for this gas (*this temperature being always higher than the critical temperature*).

If air is being liquefied, it is first freed from carbon dioxide and water vapour by being passed through caustic soda, since during the process these would solidify and check the pipes. It is then compressed to about 200 atmospheres by the pump *P* as shown in the Fig. 10.7 and the heat of compression is removed in the coil *C* immersed in the water bath which is at room temperature. After this,

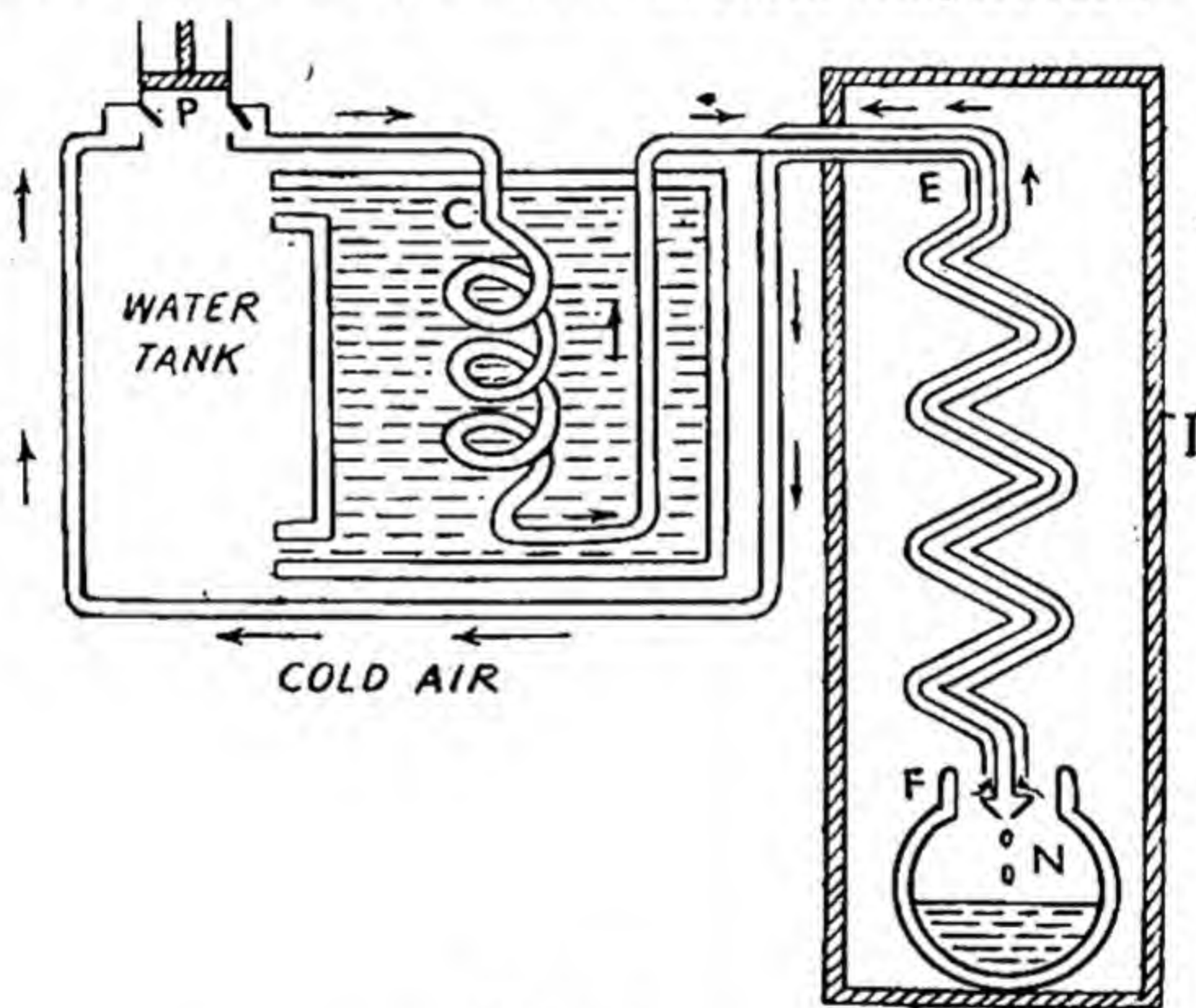


Fig. 10.7.

the gas passes through a spiral in the heat exchanger and expands through nozzle *N*, the aperture of which can be controlled from outside the exchanger. This produces cooling, and the cool air passes up through the outer tube of the spiral to the pump *P*. The spiral *E* is progressively cooled, and cools the air approaching the nozzle until the temperature is reduced below the critical value, when the pressure is sufficient to liquefy the air which then collects in the Dewar flask *F*. Heat gain from outside is reduced by the heavy lagging of insulating material *I* which surrounds the heat exchanger.

Hydrogen and helium can be liquefied by this process, since their inversion temperatures are much higher than their critical temperatures and there is no difficulty in reaching the temperature at which the Linde process will operate.

3. Claude Process. The air liquefier depending on the Joule Thomson effect is a somewhat inefficient arrangement thermodynamically and in 1902 Claude devised an apparatus in which the compressed gas is allowed to expand adiabatically in an expansion engine and consequently does external work. In this case there is cooling due to the external work done in addition to the cooling due to the Joule-Thomson effect. Further more the external work can be employed in helping to drive the compression pump.

As shown in Fig. 10.8 the compressed gas, purified and precooled to room temperature, passes down the tube *A* and part of it is allowed to expand in *B* driving the piston and so doing work thereby cooling to a low temperature. This cooled gas at low pressure is sent back to the condenser *C* where it cools the down coming high pressure gas on leaving *C*. the low pressure gas is conveyed back to the

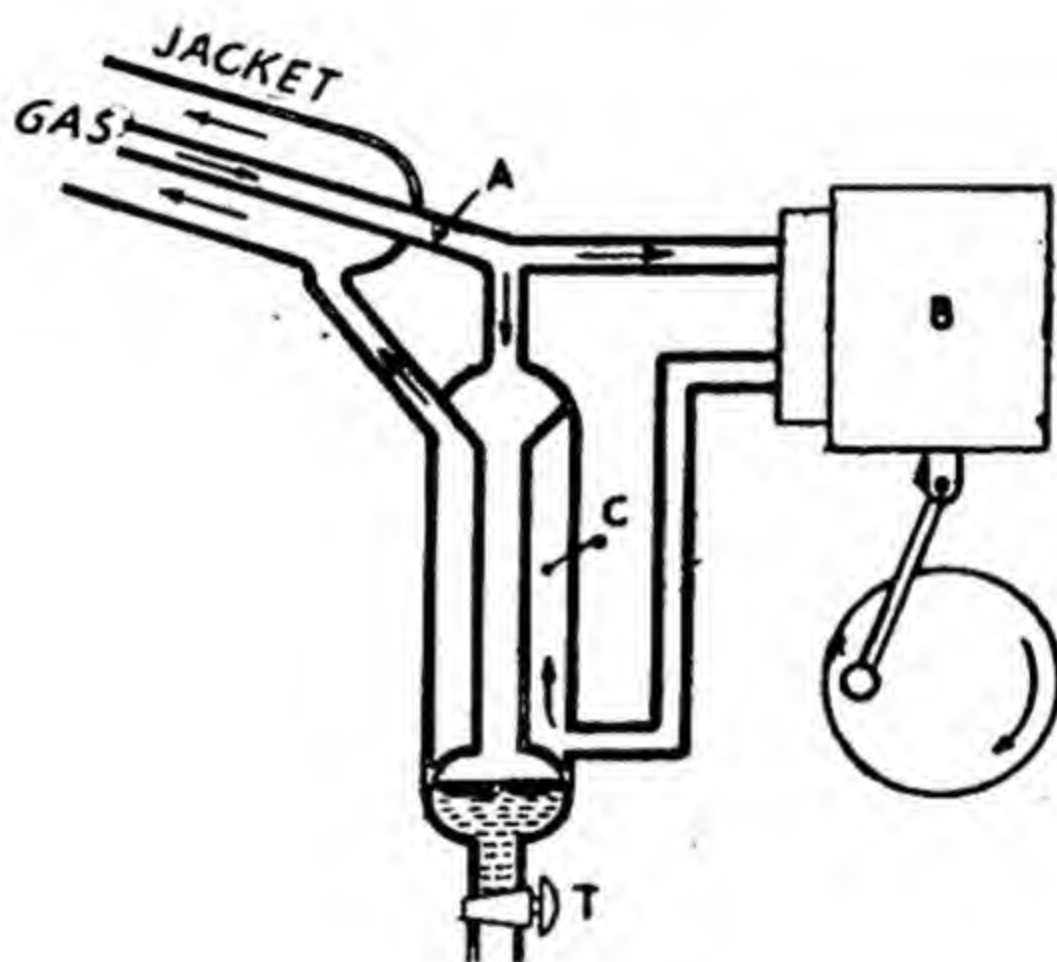


Fig. 10.8

compressor via the jacket where it cools the incoming gas also. In this way, the gas is progressively cooled to lower and lower temperature until its temperature falls to a value below its critical temperature. When it starts liquefying under the incoming pressure. The resulting liquid can then be drawn off by means of a tap *T* from the bottom of the condenser *C*.

It is difficult to find suitable lubricants for these low temperatures, although Claude found petroleum ether to be suitable for his work. In practice the method is not nearly as efficient as would be theoretically predicted and most commercial liquefiers use the Linde process since it is only slightly less efficient, is mechanically simpler and requires no lubricants.

10.9. Refrigerating machines. These are the machines devised for the production of artificial cold required to maintain a chamber for the

storage of perishable food or fruit at a low temperature or to keep a brine-bath well below 0°C for manufacture of ice.

The basic principle involved in these machines is the cold produced by evaporation of a liquid under reduced pressure, often in conjunction with the cooling effect produced when a gas expands adiabatically as already mentioned.

The liquids which are generally employed are :—

(i) Ammonia (It is most commonly used in large refrigerating plants as in ice factory).

(ii) Sulphur dioxide (SO_2).

(iii) Freon or dichloro-difluoro-methane ($\text{C Cl}_2 \text{ F}_2$)

The liquids (ii) and (iii) are employed in small refrigerators meant for domestic purposes. Sulphur dioxide can be more easily liquefied than ammonia or Freon, so that a less stout compressor and condensor can be used, but for producing the same cooling effect as with ammonia, the compressor has to be made large.

Two types of refrigerating machines are used in practice. These are (i) compression type (ii) Absorption type.

The essential difference between the two consists in the manner of compressing the low pressure vapour. In the first type of machine i.e., in the compression type a motor compressor is used while in the absorption type a dilute solution of the refrigerant at room temperature is used to dissolve the low pressure vapour and the concentrated solution is heated to expel the vapour at high pressure. The compression type is more efficient, requires less initial cost and hence is used much more than the absorption type. The compression type refrigerating machine is called **Frigidaire** or **vapour compression refrigerator**.

The principle of action of this type of machine is shown in Fig. 10.9.

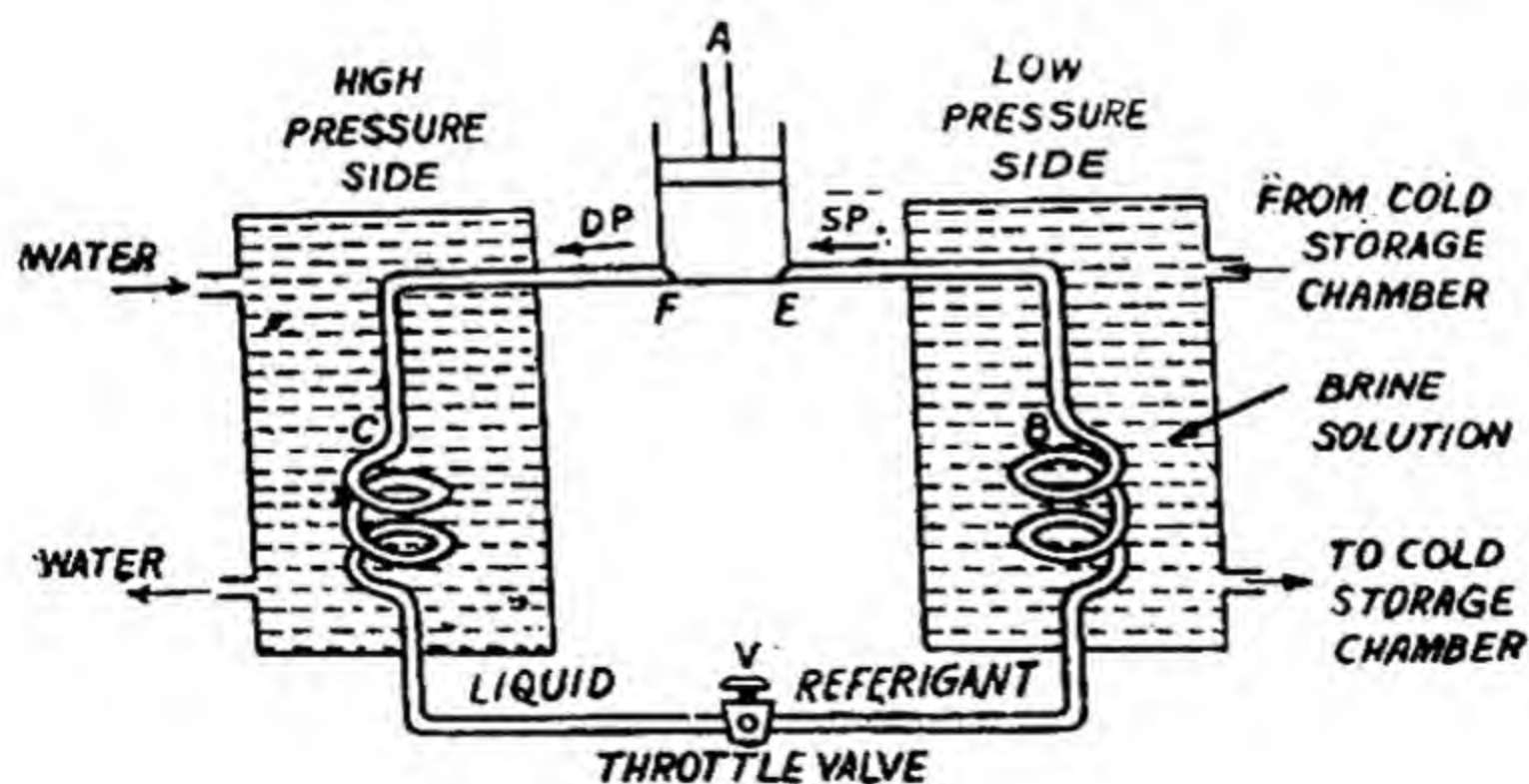


Fig. 10.9

The piston A is driven by an electric motor and is connected through

a valve E to a spiral (evaporator) in the cold bath B and through valve F to a spiral or condenser in hot bath C . The spirals are connected at the bottom by a tube and throttle valve V and contain suitable chemical such as ammonia or sulphur dioxide. In modern machine dichloro difluoro-methane (Freon) is often used.

When the piston moves upwards, the pressure in the cylinder falls below the pressure in the evaporator and as a result the valve E opens and the low pressure vapour is sucked into the pump through the suction pipe. During the downward stroke of the piston, the vapour is compressed, which closes the valve E and opens the valve F , and the compressed vapour is delivered to the condensor through the discharge pipe. The condensor C is cooled by circulating cold water and the vapour liquefies due to high pressure and lowering of temperature. The liquid refrigerant passes through the expansion or regulator valve V which reduces the pressure of the liquid from the high value prevailing in the condenser to the low value in the evaporator. Due to low pressure the liquid evaporates in B , extracting its latent heat from the cold storage space or brine water surrounding B . The space or brine water is consequently cooled. The low pressure vapour is sucked in again by the compressor and the cycle of operation is maintained,

10.10. Domestic Refrigerator. The principle of the working of a domestic

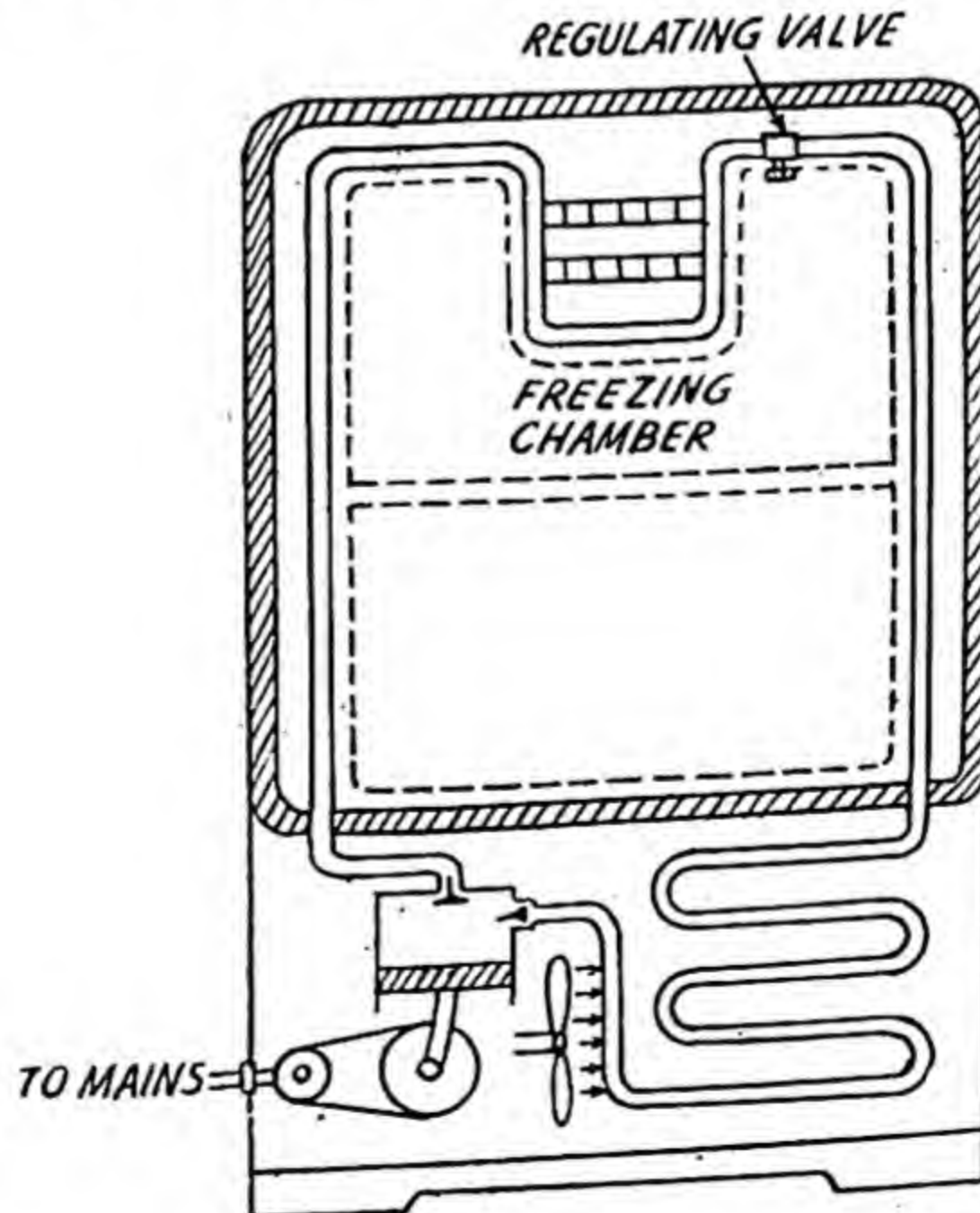


Fig. 10.10

refrigerator is similar to the ammonia ice plant. It consists of a

small double walled cabinet or box, the space between the walls is packed with a heat insulating material like glass wool. The compressor and the condensing coils are placed at the bottom of the cabinet. The evaporating coils and the regulating valve are fitted in a small chamber near the top. The gas used is **freon**, *i.e.*, di-chlorodifluoromethane. When a low pressure is created in the evaporating coils freon vaporises producing cooling. The temperature in the chamber falls below zero. This chamber is known as the freezing chamber and is used for freezing water or milk. The cooled gases leaving the freezing chamber are circulated in the rest of the cabinet thereby producing a low temperature of about 5°C . The cooling of gas in the condenser is done by circulation of air with the help of fan. A thermostat is provided in all refrigerators. This makes the working of the electric motor automatic. The motor starts as soon as the temperature rises above 5°C and stops when the temperature falls below 5°C . A refrigerator is used for storing food, blood vaccine, fruits, etc., which keep well when cold but deteriorate at ordinary room temperature.

Expected Questions

1. Give an account of the work of Andrews on the relation between the pressure, volume and temperature of a gas. Explain with the help of diagrams, the terms critical temperature and critical pressure.
2. Describe a method for determining the critical temperature.
3. Give an account of the properties of a fluid in the neighbourhood of the critical point. Define the critical constants of a fluid and describe how they are determined.
4. Give the derivation of Vander Waal's Equation of state. Discuss the significance of the equation and show how it gives the values of critical constants in terms of the constants of the equation.
5. Deduce the reduced equation of state of a gas from Van-der Waal's equation and show that if the two gases have the same reduced pressure and volume, they will have the same reduced temperature.
6. Discuss the isothermal curves relating pressure and volume for carbon dioxide for temperatures above and below the critical temperature.
7. Distinguish between a vapour and a gas.
8. Explain the physical principles that are applied to the liquifaction of gases. Describe briefly a method of producing liquid air on a large scale.
9. Describe a method for producing liquid oxygen for industrial purposes.

CHAPTER XI

THERMAL CONDUCTIVITY

Heat travels from a body at a higher temperature to a body at a lower temperature. There are three distinct processes by which heat may travel from one place to another.

1. Conduction
2. Convection
3. Radiation

11.1. Conduction. We know that heat is a form of energy possessed by a body by virtue of the vibratory motion of its particles. This concept at once helps us to understand the conduction of heat along a certain material. When one end of an iron rod is placed in fire, the molecules near this end receive some heat energy from the fire and begin to vibrate more vigorously. These molecules collide against and agitate the molecules in the next layer of the material and increase their vibratory motion. These molecules in turn, agitate the molecules in the next layer and so on till the molecules at the other end are also speeded up. Thus the heat energy in the form of kinetic energy of the molecules is passed on from one section of the rod to the other till the other end also becomes hot. This process of transmission of heat is called **conduction**. *It is that process of transmission of heat in which heat travels from particle to particle in the direction of fall of temperature, the particles themselves remaining at rest in their relative positions.* Solids are generally heated up by this process.

Some substances allow heat to pass through them more easily than others. Such substances are termed as **good conductors**. The metals as a rule are good conductors of heat, for example Silver, Copper and Aluminium are all good conductors in the order of their conductivities.

Those substances which allow heat to pass through them with great difficulty are called **bad conductors** or **insulators**. Glass, wood, bone, wool, and cork are the examples of bad conductors. As a rule liquids and gases are poor conductors but **Mercury** is the only exception.

11.2. Thermal Conductivity. Consider a cube of some material whose opposite parallel faces are maintained at different temperatures. The quantity of heat Q that flows from the face at a higher temp., θ_1 to the opposite face at a lower temperature θ_2 , is found to depend upon the following factors.

(i) It is directly proportional to A , the area of the face.

(ii) It is directly proportional to the temperature difference $(\theta_1 - \theta_2)$

(iii) It is directly proportional to the time t in seconds.

(iv) It is inversely proportional to the distance between the two faces i.e., distance x .

(v) It depends upon the nature of the material.

Then
$$Q \propto \frac{A(\theta_1 - \theta_2)t}{x}$$

or
$$Q = \frac{KA(\theta_1 - \theta_2)t}{x}$$

...(i)

Where K is a constant depending on the nature of the material of the cube and is known as its **thermal conductivity** or coefficient of **thermal conductivity** or **co-efficient of heat conduction**.

If in equation (i) above.

$$\begin{array}{ll} A = 1 \text{ sq. cm.}, & (\theta_1 - \theta_2) = 1^\circ\text{C} \\ t = 1 \text{ sec.} & x = 1 \text{ cm.}, \text{ then} \\ Q = K. \end{array}$$

Hence the coefficient of thermal conductivity of a substance is the quantity of heat that flows in one second through the opposite faces of a cube of the material having area of each face one sq. cm. and distance between the faces one cm. when the faces are maintained at a temperature difference of 1°C .

Or

It is numerically equal to the quantity of heat in calories that flows in one second through a cm. cube of a material when its opposite faces are maintained at a temperature difference of 1°C .

Re-arranging equation (i) we have

$$K = \frac{Qx}{A(\theta_1 - \theta_2)t}$$

Naturally, the units of thermal conductivity K depend on the units selected for the quantities on the R. H. S. of the above equation.

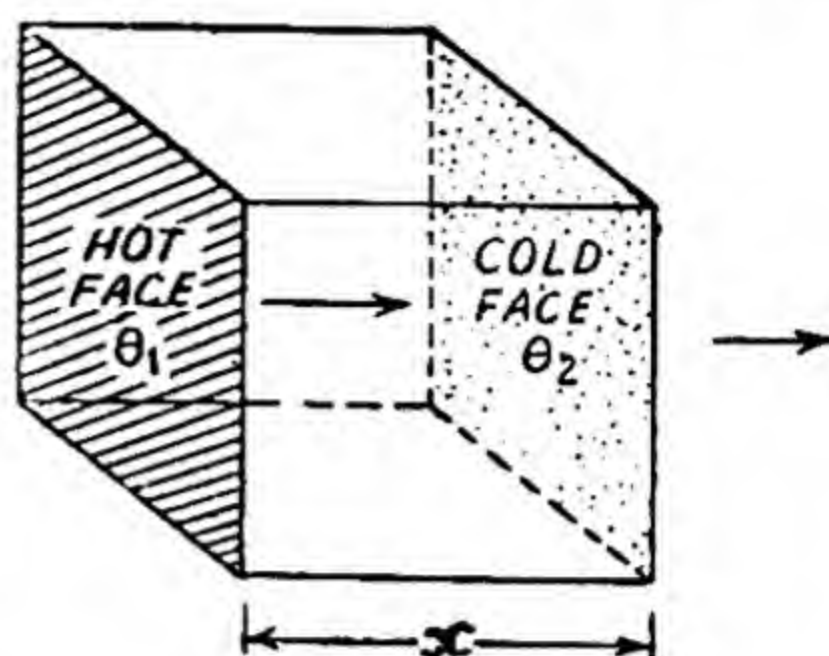


Fig 11.1.

(a) C.G.S. units

$$K = \frac{Q \text{ (cal)} \times x \text{ (cm)}}{A \text{ (sq. cm. or cm.}^2\text{)} \times (\theta_2 - \theta_1) \text{ (}^\circ\text{C)} \times t \text{ (sec)}}$$

$$= \frac{Qx}{A (\theta_2 - \theta_1)t} \cdot \frac{\text{cal}}{\text{cm. } ^\circ\text{C sec}} = \text{cal cm}^{-1} ^\circ\text{C}^{-1} \text{ sec}^{-1}$$

i.e. the units of K are **cal/cm/°C/sec.**

(b) M. K. S. units. In this system metre is denoted by m and kilocalorie by $K\text{-cal}$.

$$K = \frac{Q(K\text{-cal}) \times x \text{ (m)}}{A \text{ (m}^2\text{)} \times (\theta_1 - \theta_2) \text{ (}^\circ\text{C)} t \text{ (sec)}}$$

$$= \frac{Qx}{A (\theta_1 - \theta_2) t} \cdot \frac{K\text{-cal}}{m ^\circ\text{C sec}} = K\text{-cal m}^{-1} ^\circ\text{C}^{-1} \text{ sec}^{-1}$$

i.e., the units of K are **K-cal/m/°C/sec.**

11.3. Effect of temperature The thermal conductivities of practically all materials depend upon the temperature of the material. For some materials the thermal conductivity increases as the temperature of the material rises, for other it decreases. This variation is approximately linear over a considerable range of temperature for most materials. Thus, if the thermal conductivity is plotted against temperature a straight line is obtained as shown.

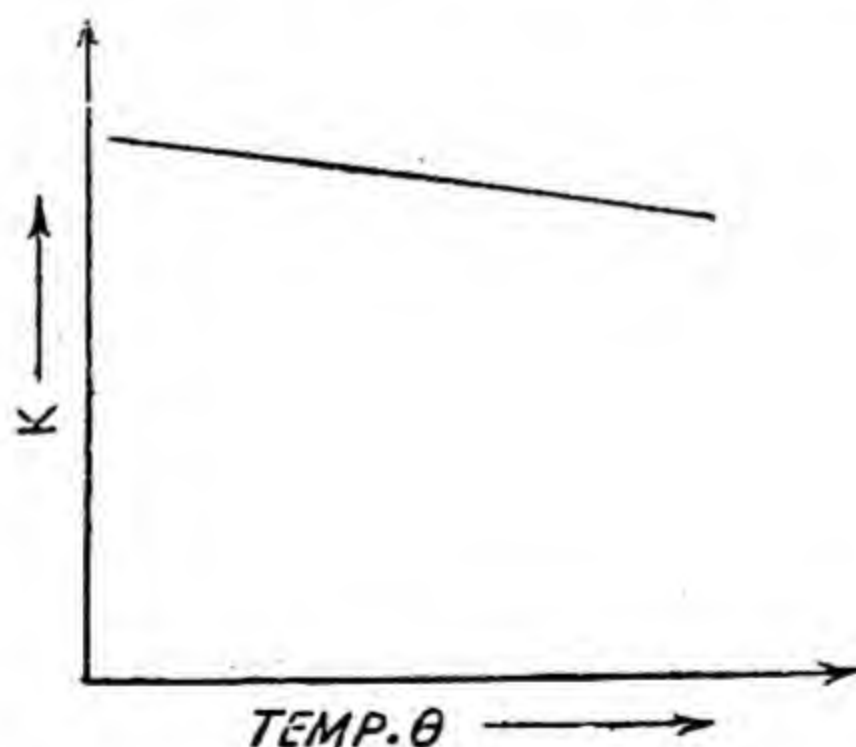


Fig. 11.2

11.4. Temperature gradient. We have seen that there is a temperature fall of $(\theta_1 - \theta_2)$ over a distance x . The quantity $\frac{\theta_1 - \theta_2}{x}$ is the rate at which temperature changes with distance in the direction in which heat flows. It is called the **temperature gradient**.

If the distance between the two faces is very small and is denoted

by dx and the difference of temperature by $d\theta$, then the limiting value of $\frac{\theta_1 - \theta_2}{x} = \frac{d\theta}{dx}$ the temperature gradient.

Hence equation (i) can be written as

$$Q = KA \frac{d\theta}{dx} t$$

Since temperature decreases as x increases, hence sometimes a negative sign is put on the right hand side of the above equation which becomes.

$$Q = -KA \frac{d\theta}{dx} t$$

The negative sign indicates that the temperature decreases as the distance x from the hot face increases.

The conduction of heat through any body is said to be *unsteady* if the temperature at any point in the body varies with time and it is said to be *steady* if the temperature at every point in the body remains constant. Hence with *unsteady* conduction the temperature gradient $\frac{d\theta}{dx}$ at each point in the body also varies with the time. With *steady* conduction the temperature gradient at each point remains constant.

For example, when steam is first admitted to a pipe covered with insulation, the temperature at the inner surface of the insulation rises very rapidly, but the temperature at any point near the outer surface is not immediately affected. The temperature at each point in the insulation continues to rise for some time, and during this period the flow of heat through the insulation is unsteady. Finally, however, the temperature at each point reaches some value at which it remains constant, the flow of heat is then steady.

11.5. Ohm's Law for heat current. There is a close similarity between the flow of heat and the flow of electricity.

(a) The electric current flowing through a wire between two points is given by,

$$i = \frac{V}{R} = \frac{\text{Potential difference between two points}}{\text{Resistance between these points}}$$

But

$$R = \frac{\rho l}{a} = \frac{l}{a\sigma}$$

Where

$$\sigma = \frac{1}{\rho} = \text{electric conductivity}$$

\therefore

$$i = \frac{V}{\frac{l}{a\sigma}}$$

...(ii)

l = length of the wire

a = area of cross-section of the wire

(b) the rate of flow of heat between two point is given by

$$q = KA \frac{(\theta_1 - \theta_2)}{x} \text{ cal/sec}$$

where $\frac{Q}{t} = q$

or $q = \frac{\theta_1 - \theta_2}{\frac{x}{KA}} \dots (iii)$

Comparing (ii) and (iii) we see that temperature difference $(\theta_1 - \theta_2)$ corresponds to potential difference V and $\frac{x}{KA}$ corresponds to electrical resistance and may be called as thermal resistance.

$$\therefore \text{heat current} = \frac{\text{Temperature difference}}{\text{Thermal resistance}}$$

In an electrical circuit if there are two or three resistances in series, then the current is given by

$$\begin{aligned} i &= \frac{V}{R_1 + R_2 + R_3} = \frac{V}{\frac{l_1}{a_1 \sigma_1} + \frac{l_2}{a_2 \sigma_2} + \frac{l_3}{a_3 \sigma_3} + \dots} \\ &= \frac{V}{\Sigma \frac{l}{a \sigma}} \end{aligned}$$

Similarly if heat conduction takes place through two or three plates of different materials then equation for heat current becomes.

$$\begin{aligned} q &= \frac{\theta_1 - \theta_2}{\frac{x_1}{A_1 K_1} + \frac{x_2}{A_2 K_2} + \frac{x_3}{A_3 K_3} + \dots} \\ &= \frac{\theta_1 - \theta_2}{\Sigma \frac{x}{AK}} \end{aligned}$$

11.6. Thermometric Conductivity or Diffusivity. In Art. 11.4 we have considered the flow of heat through a body in a steady state. In this condition the temperature of the various parts of the body remains constant. But before the steady state is reached, the rate at which a body gets heated will depend not only on the thermal conductivity but also on the thermal capacity of the body. We therefore, introduce another quantity called **thermo-metric conductivity or thermal diffusivity (h)**.

Thermometric Conductivity or (diffusivity h) is defined as the ratio of the coefficient of thermal conductivity to the thermal capacity per unit volume of the material.

If S is the specific heat and ρ the density (mass/unit volume).

then Thermal capacity per unit volume $= S \times \rho$

$$\therefore h = \frac{\text{Thermal conductivity}}{\text{Specific heat} \times \text{density}} = \frac{K}{S \times \rho}$$

Example 1. A boiler is made of iron plates 1.2 cm. thick. If the temperature of the outer surface be 120°C and that of the inner 100°C , calculate the mass of water evaporated per hour, assuming the area of the heating surface to be 50,000 sq. cm., K for iron $= 0.2$ C.G.S. units.

$$\begin{aligned} \text{Heat transferred per hour } Q &= \frac{KA (\theta_1 - \theta_2) t}{x} \text{ calcs.} \\ &= \frac{0.2 \times 50,000 (120 - 100) \times 60 \times 60}{1.2} \\ &= 6 \times 10^8 \text{ calcs.} \end{aligned}$$

Heat required to evaporate one gm. of water at 100°C is equal to its latent heat $= 540$ calcs.

$$\begin{aligned} \therefore \text{mass of water evaporated per hour} &= \frac{6 \times 10^8}{540} \\ &= 1.11 \times 10^6 \text{ gms.} \end{aligned}$$

Example 2. A slab of thermal insulator is 100 cm^2 in cross-section and 2 cm. thick. Its thermal conductivity is $2 \times 10^{-4} \text{ cal. cm}^{-1} \text{ sec}^{-1} \text{ }^\circ\text{C}^{-1}$. If the temperature difference between the opposite faces is 100°C , how many calories flow through the slab per day?

$$Q = \frac{KA (\theta_1 - \theta_2) t}{x}$$

Substituting the values of various quantities in the formula, we get

$$\begin{aligned} Q &= \frac{2 \times 10^{-4} \times 100 \times 100 \times 24 \times 3600}{2} \\ &= 86400 \text{ calcs.} \\ &= 86.4 \text{ K. cal.} \end{aligned}$$

Example 3. A boiler is made of a copper plate 2.4 mm thick coated inside with a layer of tin 0.2 mm thick. Surface area exposed to hot gases at 700°C is 100 sq. cm. Calculate the maximum amount of steam that could be raised per hour at atmospheric pressure. Conductivities of Copper

and tin are 0.9 and 0.15 c.g.s. units respectively. Latent heat of steam at normal pressure is 540 cal/gm.

Heat is conducted through the copper plate and the coating of tin connected in series

$$\begin{aligned} \text{Heat transferred } Q &= \frac{\frac{d\theta}{\Sigma x}}{\frac{KA}{K}} \times t = \frac{Ad\theta}{\Sigma x} \times t \\ &= \frac{100 \times (700 - 100) \times 60 \times 60}{\frac{0.24}{0.9} + \frac{0.02}{0.15}} = 540 \times 10^6 \text{ Cals,} \end{aligned}$$

Heat required to convert 1 gm of water at 100°C into steam = 540 Cals.

\therefore Maximum mass of water evaporated per hour

$$= \frac{540 \times 10^6}{540} = 10^6 \text{ gms.}$$

Example 4. A slab consists of two parallel layers of different materials 4 cms and 2 cms thick and of thermal conductivity of 0.54 and 0.36 c.g.s. units respectively. If the opposite faces of the slab are at 100°C and 0°C , calculate the temperature of the interface.

Let the temperature of the common surface be $\theta^\circ\text{C}$.

$$\therefore \frac{K_1 A (\theta_2 - \theta) t}{x_1} = \frac{K_2 A (\theta_2' - \theta_1) t}{x_2}$$

$$\frac{0.54 \times A (100 - \theta) t}{4} = \frac{0.36 A (\theta - 0) t}{2}$$

$$0.36 \theta = \frac{2 \times 0.54 (100 - \theta)}{4}$$

$$\text{or } 0.72 \theta = 0.54 (100 - \theta)$$

$$\text{or } 72 \theta = 54 (100 - \theta)$$

$$\text{or } 72 \theta + 54 \theta = 54 \times 100$$

$$\text{or } \theta = \frac{54 \times 100}{(72 + 54)} = \frac{5400}{126} = 42.86^\circ\text{C}$$

Example 5. Equal bars of copper and aluminium are welded end to end and lagged. If the free ends of copper and aluminium are maintained at 100°C and 0°C respectively, find the temperature of the welded interface. Assume the thermal conductivities of copper and aluminium to be 0.92 and 0.5 cal/cm/deg/sec. respectively.

Let the temperature of the welded interface be θ . As the compound bar is lagged therefore the amount of heat entering per second at the hot end is equal to the amount of heat leaving the copper bar at the interface. It is further equal to the amount of heat entering aluminium per second at the interface and leaving at the cold end. Let this be Q . If A is the area of cross-section of the bar and x the length of each

portion, then

$$\text{For Copper bar } Q = \frac{KA(\theta_1 - \theta)}{x} = \frac{0.92 A (100 - \theta)}{x}$$

For Aluminium bar

$$Q = \frac{KA(\theta - \theta_2)}{x} = \frac{0.50 A (\theta - 0)}{x}$$

$$\therefore \frac{0.92 \times A (100 - \theta)}{x} = \frac{0.50 A (\theta - 0)}{x}$$

$$\text{or } \theta = 64.8^\circ \text{C}$$

Example 6. Calculate approximately the heat passing per hour through the walls and windows of a room $5 \times 5 \times 5$ metres if the walls are of bricks of thickness 30 cms and have windows of glass 3 mm thick and total area 5 square metres. The temperature of the room is 30°C below that of the outside and thermal conductivity of bricks and of glass is 12×10^{-4} and 25×10^{-4} c.g.s. units respectively.

$$\begin{aligned} \text{Total area of the four walls including windows} \\ = 5 \times 5 \times 10^4 \times 4 = 100 \times 10^4 \text{ cm}^2 \end{aligned}$$

$$\begin{aligned} \text{Total area of all the windows} \\ = 5 \text{ m}^2 = 5 \times 10^4 \text{ cm}^2 \end{aligned}$$

$$\text{Net area of the brick walls} = 100 \times 10^4 - 5 \times 10^4 = 95 \times 10^4 \text{ cm}^2$$

$$\text{Time} = 1 \text{ hour} = 3600 \text{ seconds.}$$

$$\text{Temperature difference between inside and outside} = 30^\circ \text{C.}$$

$$\text{Conductivity of bricks} = 12 \times 10^{-4} \text{ c.g.s. units}$$

$$\text{Thickness of walls} = 30 \text{ cm.}$$

$$\begin{aligned} \text{Heat passing through the walls } Q_1 &= \frac{KA(\theta_1 - \theta_2)t}{x} \\ &= \frac{12 \times 10^{-4} \times 95 \times 10^4 \times 30 \times 3600}{30} \\ &= 4104 \times 10^4 \text{ cal.} \end{aligned}$$

$$\text{Thickness of glass.} = 3 \text{ mm} = 0.3 \text{ cm.}$$

$$\text{Conductivity of glass} = 25 \times 10^{-4} \text{ c.g.s. units.}$$

Heat passing through the glass window

$$Q_2 = \frac{25 \times 10^{-4} \times 5 \times 10^4 \times 30 \times 3600}{0.3}$$

$$\begin{aligned} \text{Total heat passing } Q &= Q_1 + Q_2 \\ &= 410.4 \times 10^4 + 4500 \times 10^4 \\ &= 4910.4 \times 10^4 \text{ Cals.} \end{aligned}$$

11.7. Formation of ice on the surface of a pond. There is formation of ice on the surface of a pond because of the extraction of heat from water. When ice first begins to form on a pond, this is because of the removal of the latent heat from a thin layer of surface water at 0°C by the comparatively cold air layer above it. For further increase in the thickness of the ice layer the latent heat is drawn from the unfrozen water by conduction through the ice layer already formed. Hence heat passes from water below the ice layer to the cold air above it.

Let x cm. be thickness of the layer of ice, t seconds after the

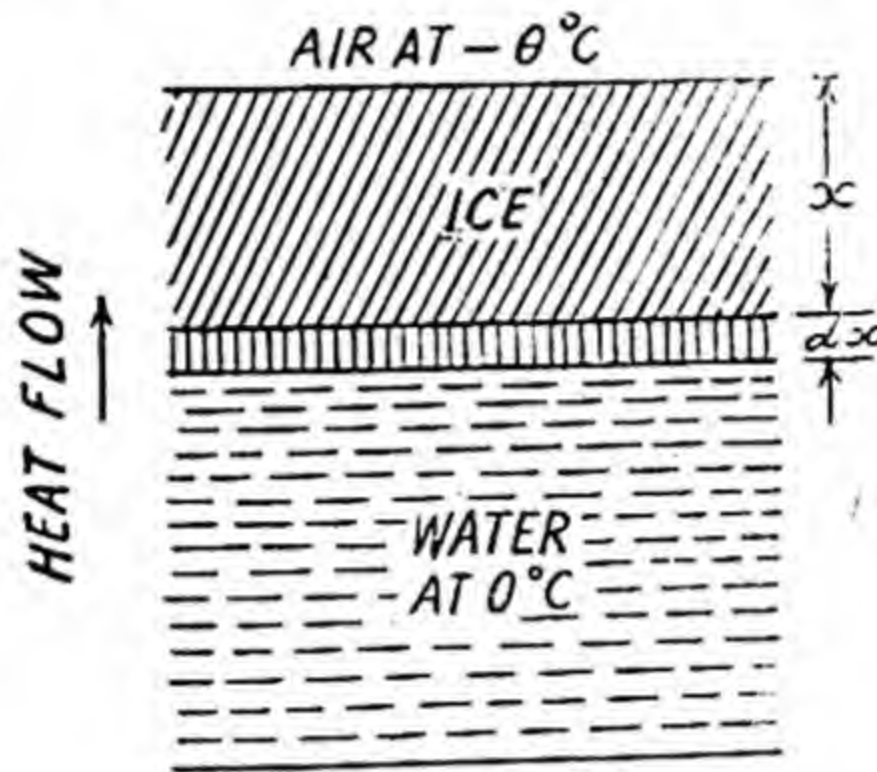


Fig. 11.3.

formation of the ice starts.

Let the thickness increase by an amount dx after a further time interval of dt second.

If a sq. cm. is the area of the surface, and ρ is the density of ice in gm./c.c., the mass of the ice formed in the layer of thickness

$$dx = a \, dx \, \rho \text{ gm.}$$

$$\text{Heat lost by water} = a \, dx \cdot \rho \, L \text{ cal.} \quad \dots(i)$$

where L is the latent heat of fusion of ice

This heat is conducted through the ice layer already present.

$$\therefore \text{amount of heat conducted} = K a \frac{\theta}{x} dt \text{ cal.} \quad \dots(ii)$$

where $\frac{\theta}{x}$ is the temperature gradient through the ice and $-\theta^\circ\text{C}$

is the temperature of the air above the pond surface.

From equation (i) and (ii) we have

$$a \rho \, dx \, L = K \, A \frac{\theta}{x} dt \quad \dots(iii)$$

(i) Rate of increase of thickness of the ice layer as found from

equation (iii) is

$$\frac{dx}{dt} = \frac{K}{\rho L} \cdot \frac{\theta}{x} \quad \dots(iv)$$

(ii) and the time required for increase of thickness dx is

$$dt = \frac{\rho L}{K\theta} \cdot x \, dx.$$

If x_1 is the initial thickness of ice layer t_1 sec. after the commencement of the formation and x_2 is the thickness after t_2 sec., then by integrating both sides, we have

$$\int_{t_1}^{t_2} dt = \frac{\rho L}{K\theta} \int_{x_1}^{x_2} x \, dx$$

$$t_2 - t_1 = \frac{1}{2} \frac{\rho L}{K\theta} (x_2^2 - x_1^2)$$

The time required to increase the thickness from x_1 to x_2 is.

$$t = \frac{1}{2} \frac{\rho L}{K\theta} (x_2^2 - x_1^2)$$

And time required to deposit a layer of thickness x from the commencement of ice formation.

$$= \frac{1}{2} \frac{\rho L}{K\theta} x^2.$$

Example 7. A pond is covered by a layer of ice 1 cm. thick, the temperature of the upper and lower surface of ice layer being respectively -10°C and 0°C . Find the time taken to deposit the next 1 m.m. layer of ice $K=0.004$ c.g.s. units, ρ of ice $=0.928$ gm./cm³. (Aero Society)

The time t take by ice layer to increase in thickness from x_1 to x_2 is given by

$$t = \frac{1}{2} \frac{\rho L}{K\theta} (x_2^2 - x_1^2)$$

where ρ , l , K and θ have their usual meanings.

Substituting the various values, we have

$$t = \frac{1}{2} \frac{0.928 \times 80}{0.004 \times 10} (1.1^2 - 1^2)$$

$$= 192 \text{ seconds} = 3.2 \text{ minutes}$$

Example 8. Calculate the rate of increment of the thickness of ice layer on a lake when the thickness of ice is 20 cms. and the air temperature is -40°C . Thermal conductivity of ice $=0.004$ cal/cm/sec/ $^\circ\text{C}$, density

of ice = 0.92 gm./c.c. and its latent heat of fusion 80 cal/gm. After what time the thickness will be doubled.

Rate of increase of thickness of the layer is given by

$$\frac{dx}{dt} = \frac{K}{\rho L} \cdot \frac{\theta}{x}$$

Where $\frac{\theta}{x}$ is the temperature gradient through the ice and $-\theta^\circ\text{C}$ is the temperature of the air above the lake surface.

Temperature of air (atmosphere) $\theta_1 = -40^\circ\text{C}$

Temperature of water $\theta_2 = 0^\circ\text{C}$

$$\therefore \theta = \theta_2 - \theta_1 = 0 - (-40^\circ\text{C}) = 40^\circ\text{C}$$

Thickness of ice $x = 20$ cms.

$$\therefore \frac{dx}{dt} = \frac{K}{\rho L} \cdot \frac{\theta}{x} = \frac{0.004 \times 40}{0.92 \times 80 \times 20} = 1.08 \times 10^{-4} \text{ cm./sec.}$$

To find the time in which the layer of ice will be doubled i.e., will increase from 20 cm. to 40 cm. substitute the values of the quantities given in the relation.

$$t = \frac{1}{2} \frac{\rho L}{K \theta} (x_2^2 - x_1^2)$$

$$\therefore t = \frac{1}{2} \frac{0.92 \times 80 (40^2 - 20^2)}{0.004 \times 40 \times 60 \times 60} = 76 \text{ hrs. 40 minutes.}$$

Example 9. Calculate the time in which a layer of ice on the surface of a pond which is already 3 cm thick will increase in thickness by 1 mm. The temperature of air above the pond = -20°C

The time t in which the layer of ice increases from a thickness

$$x_1 \text{ to } x_2 \text{ is given by } t = \frac{1}{2} \frac{\rho L}{K \theta} (x_2^2 - x_1^2)$$

where ρ , L , K and θ have their usual meaning.

Substituting the values of various quantities given, we have

$$t = \frac{1}{2} \times \frac{0.91 \times 80}{0.005 \times 20} (3.1^2 - 3^2) \text{ sec.}$$

$$= 222 \text{ seconds} = 3 \text{ minutes and } 42 \text{ seconds.}$$

11.8. Conduction of heat through several bodies in series. Furnace walls, the insulation on high temperature piping, and many other types of equipment are frequently constructed of layers of several different kinds of materials through which heat flows in series by conduction. Take the case of a brick kiln wall. The inner layer consists of a fire

brick core of insulating brick and an outer layer of red brick. The fire brick is used to protect the insulating brick from mechanical abrasion and from the high temperatures existing within the kiln. The red brick is cheaper than the insulating brick but has a higher thermal conductivity and can not be used at the high temperatures existing at the centre of the wall.

The rate of heat transfer by conduction through such composite bodies can be calculated as follows. A compound slab consisting of two materials having different thicknesses and thermal conductivities is shown in Fig 11.4.

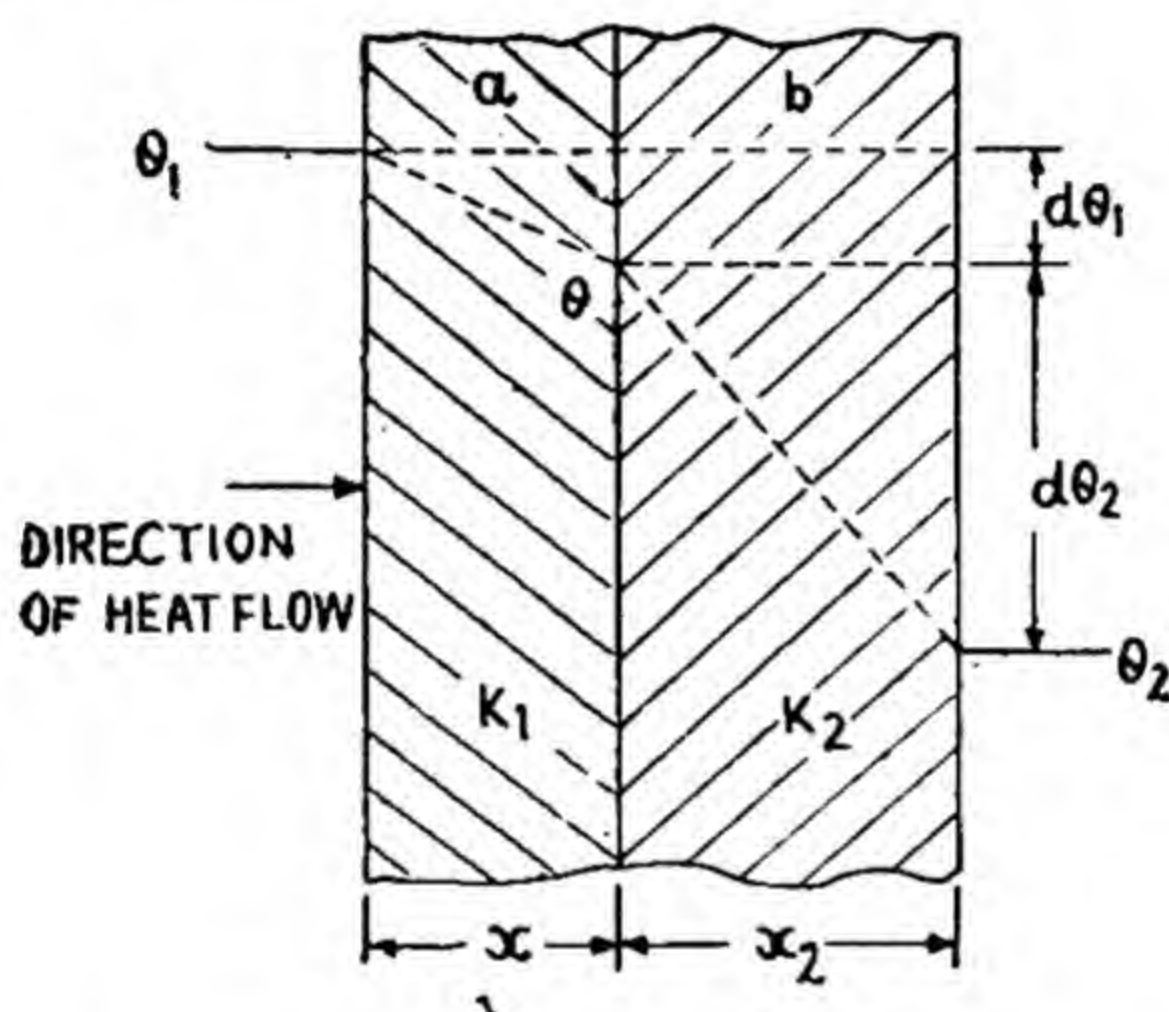


Fig. 11.4

The rate of flow of heat through section *a* is given by

$$q = \frac{K_1 A (\theta_1 - \theta)}{x_1} \quad \dots(i)$$

where $\theta_1 - \theta$ = temperature fall in the section *a*.

Under steady conditions the rate of heat transfer through section (b) is also the same (because these are in series) and is given by

$$q = \frac{K_2 A (\theta - \theta_2)}{x_2} \quad \dots(ii)$$

$$\therefore \frac{K_1 A (\theta_1 - \theta)}{x_1} = \frac{K_2 A (\theta - \theta_2)}{x_2}$$

$$\text{or } [\theta_1 - \theta] = \frac{x_1}{x_2} \cdot \frac{K_2}{K_1} \cdot A [\theta - \theta_2]$$

$$\text{or } \theta_1 - \theta = \frac{x_1}{K_1} \cdot \frac{K_2}{x_2} \cdot \theta - \frac{x_1}{K_1} \cdot \frac{K_2}{x_2} \theta_2$$

$$\text{or } \theta_1 + \theta_2 \frac{x_1}{K_1} \cdot \frac{K_2}{x_2} = \theta \left[1 + \frac{x_1}{K_1} \cdot \frac{K_2}{x_2} \right]$$

$$\text{or } \theta = \frac{\theta_1 + \theta_2 \frac{x_1}{K_1} \cdot \frac{K_2}{x_2}}{\left(1 + \frac{x_1}{K_1} \cdot \frac{K_2}{x_2}\right)}$$

Substituting the value of θ in either of the equations (i) or (ii) we have

$$q = K_2 A \left[\frac{\theta_1 + \theta_2 \frac{x_1}{K_1} \cdot \frac{K_2}{x_2} - \theta_2}{\left(1 + \frac{x_1}{K_1} \cdot \frac{K_2}{x_2}\right)} \right] \frac{1}{x_2}$$

$$\therefore q = \frac{K_2 A}{x_2} \left[\frac{\theta_1 + \theta_2 \frac{x_1}{K_1} \cdot \frac{K_2}{x_2} - \theta_2 - \theta_2 \frac{x_1}{K_1} \cdot \frac{K_2}{x_2}}{\left(1 + \frac{x_1}{K_1} \cdot \frac{K_2}{x_2}\right)} \right]$$

$$\text{or } q = \frac{K_2 A}{x_2} \left[\frac{\theta_1 - \theta_2}{\left(1 + \frac{x_1}{K_1} \cdot \frac{K_2}{x_2}\right)} \right] = \frac{K_2 A (\theta_1 - \theta_2)}{x_2 + \frac{x_2 x_1}{K_1} \cdot \frac{K_2}{x_2}}$$

$$\text{or } q = \frac{A(\theta_1 - \theta_2)}{\frac{x_2}{K_2} + \frac{x_1}{K_1}}$$

$$\text{or } q = \frac{\theta_1 - \theta_2}{\frac{x_1}{K_1 A} + \frac{x_2}{K_2 A}} = \frac{\theta_1 - \theta_2}{\frac{\Sigma x}{KA}} \quad \dots (ii)$$

Where q = the rate of heat transfer by conduction in K —cal/sec or cal/sec.

K_1 and K_2 = the thermal conductivities of materials a and b evaluated at the average temperature of each in K —cal/m/°C/sec or cal/cm/°C/sec.

θ_1 and θ_2 = the temperatures at the outside faces of the composite body in °C.

A = the cross-sectional area of the bodies taken normal to the direction of heat flow in sq. metre or sq. cm.

x_1 and x_2 = the thicknesses of materials a and b in metres or cms.

This equation can be extended to include any number of flat bodies in series by adding additional $\frac{x}{KA}$ terms to the denominator of equation (iii).

11.9. Heat conduction through the walls of a thick cylindrical pipe.
The section of a cylindrical pipe of length l whose thermal

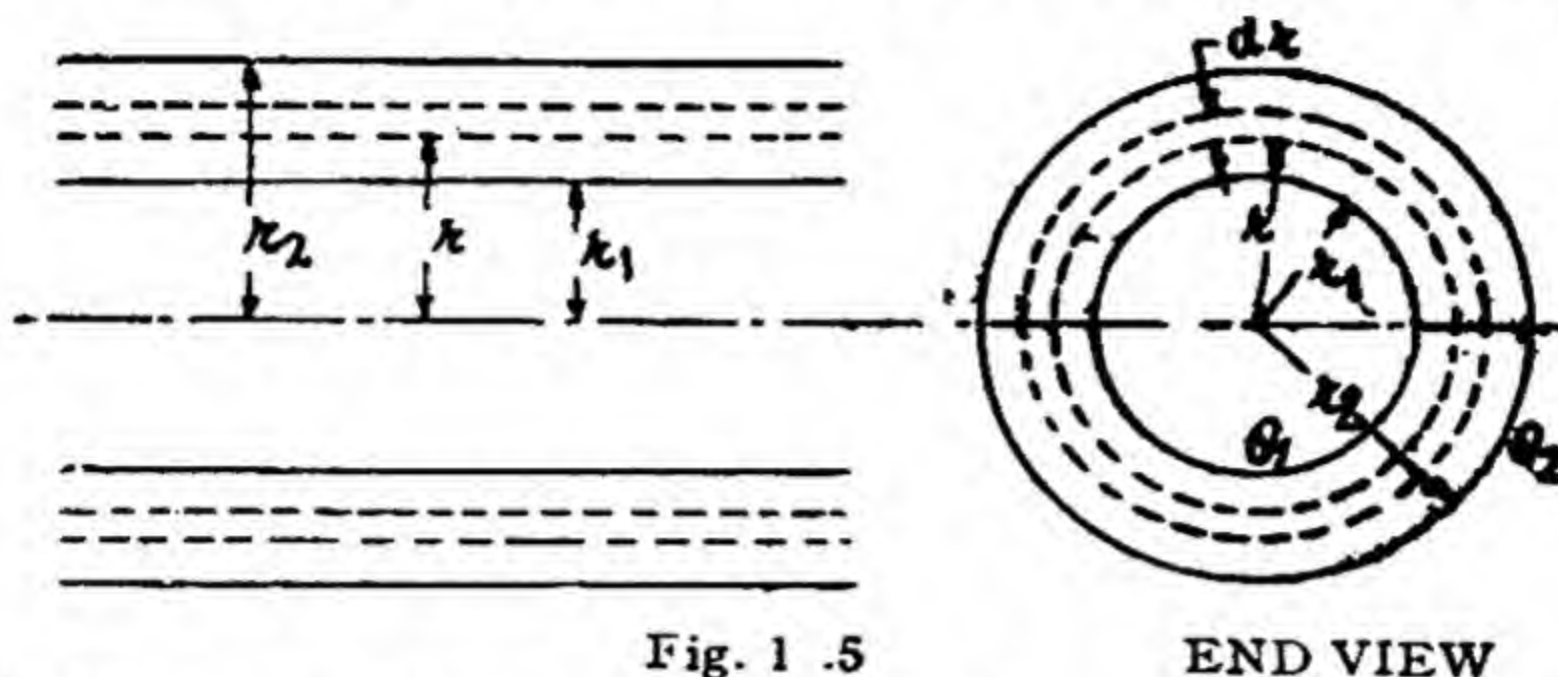


Fig. 11.5

END VIEW

conductivity is K and inner and outer radii are r_1 and r_2 respectively is shown in Fig. 11.5. Let the pipe carry steam or some hot liquid at temperature θ_1 and let the temperature of its surroundings be θ_2 . This thick pipe can be supposed to consist of a large number of thin coaxial cylinders of increasing radii as shown in the end view. It is further assumed that heat is flowing radially across the walls of the pipe.

Consider a thin cylindrical shell of thickness dr at a distance r from the axis. Let the temperature drop across thickness dr be $d\theta$. Then the rate of heat conduction through this shell per second is given by

$$q = -KA \left(\frac{d\theta}{dr} \right) = -K 2\pi r l \frac{d\theta}{dr}$$

where A = surface area of the cylindrical shell.

The above relation can be written as

$$q \frac{dr}{r} = -K 2\pi l d\theta.$$

Integrating both sides between their respective limits, we have

$$q \int_{r_1}^{r_2} \frac{dr}{r} = -2\pi K l \int_{\theta_1}^{\theta_2} d\theta$$

In the steady state q becomes constant since the quantity of heat flowing per second across any thickness of the cylinder is the same.

$$\therefore q \log_e \frac{r_2}{r_1} = -2\pi K l (\theta_2 - \theta_1)$$

$$\text{or } q = \frac{2\pi K l (\theta_1 - \theta_2)}{\log_e \frac{r_2}{r_1}}$$

or
$$q = \frac{2\pi K l (\theta_1 - \theta_2)}{2.3 \log_{10} \frac{r_2}{r_1}}$$

or
$$K = \frac{2.3 \log_{10} \frac{r_2}{r_1}}{2\pi l (\theta_1 - \theta_2)}$$

where q = the rate of heat transfer by conduction from the inner to the outer surface of the cylindrical thick pipe in K —cal/sec or cal/sec.

K = the thermal conductivity of the material of the thick pipe in K -cal/m/°C/sec or cal/cm/°C/sec.

l = length of the thick cylindrical pipe.

θ_1 and θ_2 = the temperatures at the inside and outside of the thick pipe.

r_1 and r_2 = the radii of inside and outside faces of the thick pipe.

The examples of such cases are heat transfer through boiler tubes or refrigerator pipes or through bare steam pipes etc. If the conduction of heat is steady then the rate of heat trans-

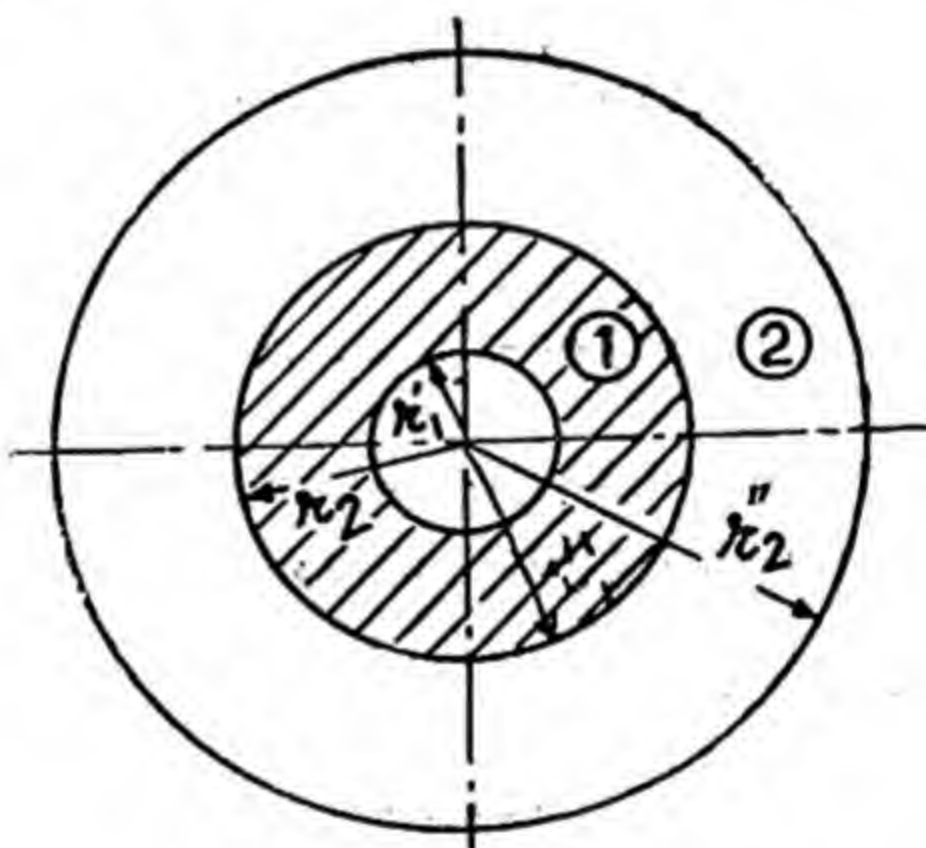


Fig. 11.6

fer through two cylindrical bodies in series (thermal contact) can be calculated by the equation.

$$q = \frac{2\pi l (\theta_1 - \theta_2)}{2.3 \left[\frac{\log \frac{r_1''}{r_1'}}{K_1} + \frac{\log \frac{r_2''}{r_2'}}{K_2} \right]}$$

The equation can be extended to include the number of concentric cylindrical bodies in series (thermal contact) by adding additional $\frac{1}{K} \log_{10} \frac{r''}{r'}$ terms to the denominator and the relation can be stated in the form

$$q = \frac{2\pi l (\theta_1 - \theta_2)}{\Sigma 2.3 \log_{10} \frac{r''}{r' K}}$$

where q = rate of heat transfer by conduction from the inner to the outer surface in K -cal/sec. or cal/sec.

K_1 and K_2 = thermal conductivities of material (1) and (2) evaluated at the average temperature of each in K -cal/m/°C/sec or cal/cm/°C / sec.

l = length of the cylinders in metres or cms.

θ_1 and θ_2 = the temperatures at the inside and outside faces of the composite body in °C.

r_1' and r_1'' = the radii of the inside and outside faces of material (1) in metres or in cms.

r_2' and r_2'' = the radii of the inside and the outside faces of material (2) in metres or in cms.

Example 10. Heat is conducted through a compound plate composed of the parallel plates of different materials A and B of conductivities 0.32 and 0.14 and each of thickness 3.6 and 4.2 cm. respectively. If the temperature of the outer faces of slab A and that of slab B are found to be steady at 96°C and 8°C respectively, find the temperature of interface A and B and also the temperature gradients in A and B .

Let the temperature of interface $A-B$ be $\theta^\circ\text{C}$ as shown in Fig. 11.6

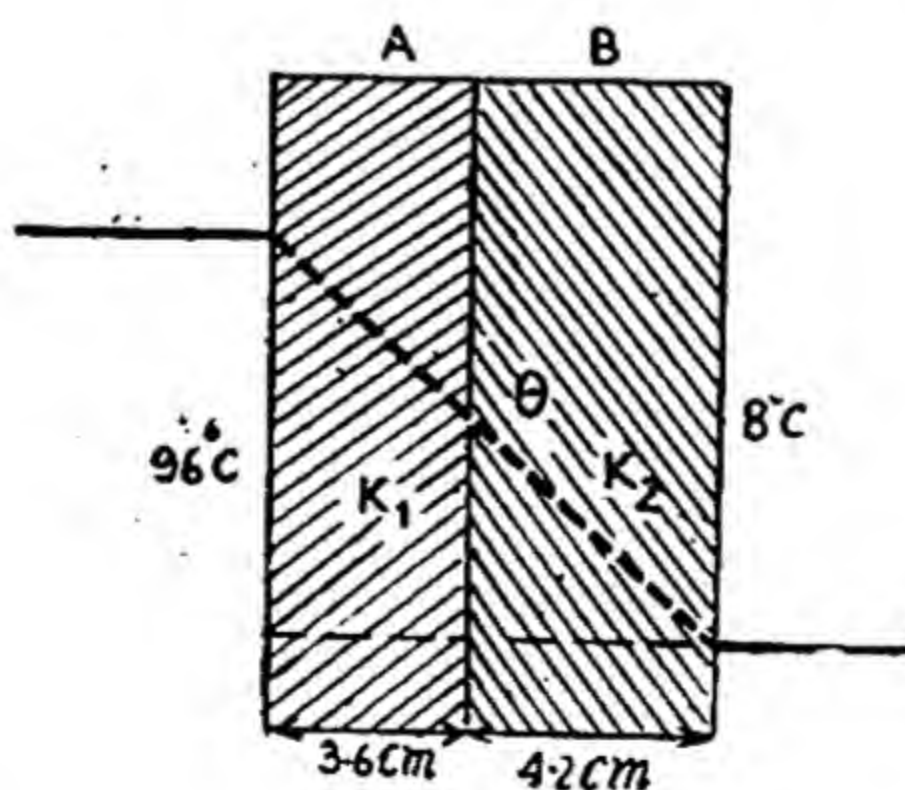


Fig. 11.6

$$\begin{aligned} \text{Rate of heat flow through } A &= \frac{K_1 A (\theta_1 - \theta)}{x_1} \\ &= \frac{0.32 A (96 - \theta)}{3.6} \text{ cal/sec.} \quad \dots(i) \end{aligned}$$

$$\begin{aligned} \text{Rate of heat flow through } B &= \frac{K_2 A (\theta - \theta_2)}{x_2} \\ &= \frac{0.14 A (\theta - 8)}{4.2} \text{ cal/sec.} \quad \dots(ii) \end{aligned}$$

where A is the area of the plate. Under steady conditions, the rate of heat flow through the plates is the same. Therefore, equating (i) and (ii) we have

$$\frac{0.32 A (96 - \theta)}{3.6} = \frac{0.14 A (\theta - 8)}{4.2}$$

$$\theta = 72^\circ\text{C}$$

\therefore Fall of temperature in
Thickness of $A = 3.6$ cms.

$$A = 96 - 72 = 24^\circ\text{C}.$$

$$\therefore \text{Temperature gradient in } A = \frac{24}{3.6} = 6.67^\circ\text{C/cm}.$$

$$\text{Similarly temperature gradient in } B = \frac{72 - 8}{4.2} = 15.4^\circ\text{C/cm}.$$

Example 11. The walls of a room consist of parallel layers in contact of cement, brick and wood of thickness 2, 30 and 1 cm. respectively. Find how much heat passes by conduction through each sq. metre of the wall per minute if the temperature of air in contact with the wall are 5°C inside and 30°C outside. The coefficients of thermal conductivities for cement, brick and wood are 0.0007, 0.006 and 0.0004 c.g.s. units respectively. (A.M.I.E)

Rate of flow of heat through the compound wall

$$Q = \frac{(\theta_1 - \theta_2)}{\Sigma \frac{x}{KA}}$$

$$= \frac{A (\theta_1 - \theta_2)}{\frac{x_1}{K_1} + \frac{x_2}{K_2} + \frac{x_3}{K_3}} \text{ cal/sec.}$$

Heat flowing per minute

$$= \frac{A (\theta_1 - \theta_2)}{\frac{x_1}{K_1} + \frac{x_2}{K_2} + \frac{x_3}{K_3}} \times 60 \text{ Cals.}$$

$$\begin{aligned} &= \frac{10^4 (30 - 5)}{\frac{2}{0.0007} + \frac{30}{0.006} + \frac{1}{0.0004}} \\ &= 1462.5 \text{ cals.} \end{aligned}$$

Example 12. A boiler plate is made of copper plate of 2.4 mm thickness coated inside with a layer of tin 0.2 mm thick. Surface area exposed to hot gases at 700°C is 100 sq. cm. Calculate the maximum amount of steam that could be raised per hour at atmospheric pressure. Conductivities

of Copper and tin are 0.9 and 0.15 c.g.s. units respectively. Latent heat of steam at normal pressure is 540 cal/gm. (A.M.I.E.)

Rate of flow of heat through the compound plate consisting of copper and tin,

$$Q = \frac{A (\theta_1 - \theta_2)}{\frac{x_1}{K_1} + \frac{x_2}{K_2}} \text{ cal/sec.}$$

Heat transmitted per hour from the hot gases to water through the compound plate, assuming the temperature of water to be 100°C .

$$\begin{aligned} &= \frac{A (\theta_1 - \theta_2)}{\frac{x_1}{K_1} + \frac{x_2}{K_2}} \times 3600 \text{ cal} \\ &= \frac{100 (700 - 100)}{\frac{0.24}{0.9} + \frac{0.02}{0.15}} \\ &= 540 \times 10^6 \text{ cal/hour.} \end{aligned}$$

Heat required for evaporation of 1 gm of boiling water = 540 cal.

\therefore Maximum amount of water evaporated per hour

$$= \frac{540 \times 10^6}{540} = 10^6 \text{ gms.}$$

Example 13. Three slabs of 25 sq. cm. in cross-section and 2.5 cm thick are piled one on the top of the other. Their thermal conductivities are 0.1, 0.2 and 0.4 c.g.s. units respectively, what is the thermal conductivity of a single slab of 6 sq. cm. in cross-section and 3 cm. thick which conducts the same heat per sec. with the same temperature difference between its faces.

For having the same temperature differences, heat conducted/sec would be equal only when thermal resistances are the same in both cases i.e.,

$$\Sigma \frac{x_i}{KA} = \frac{x}{KA}$$

$$\therefore \frac{x_1}{K_1 A} + \frac{x_2}{K_2 A} + \frac{x_3}{K_3 A} = \frac{x}{KA}$$

$$\text{or } \frac{2.5}{0.1 \times 25} + \frac{2.5}{0.2 \times 25} + \frac{2}{0.4 \times 25} = \frac{3}{K \times 6}$$

$$\text{or } 1 + \frac{1}{2} + \frac{1}{4} = \frac{1}{2K}$$

$$\text{or } 2K + K + \frac{1}{2}K = 1$$

$$\text{or } 3.5 K = 1$$

$$\therefore K = \frac{1}{3.5} = 0.286$$

Example 14. Water is pumped through an iron tube 2 metres long at the rate of 100 litres/sec. The inner and outer diameters of the tube are 5 and 6 cm respectively. The outside of the tube is surrounded by hot gases at a constant temperature of 500°C . If the temperature of water as it enters is 30°C , calculate the rise in temperature as it leaves the tube. K for iron $= 0.15$ c.g.s. units. (A.M.I.E.)

This is an example of cylindrical pipe and the quantity of heat flowing in this pipe, $Q = \frac{2\pi Kl(\theta_1 - \theta_2)}{2.303 \log_{10} \frac{r_2}{r_1}}$

Thermal conductivity $K = 0.15$

Length $l = 2$ metres $= 200$ cms.

Inner radius $r_1 = 2.5$ cm

outer radius $r_2 = 3$ cm.

Temperature of water on entering the tube $= 30^{\circ}\text{C}$.

Temperature of water at out let $= \theta^{\circ}\text{C}$

Average temperature in the tube $= \frac{30 + \theta}{2}$

Temperature of hot gases $\theta_1 = 500^{\circ}\text{C}$.

$$\therefore Q = \frac{2\pi \times 0.15 \times 200 \left(500 - \frac{30 + \theta}{2} \right)}{2.303 \log_{10} \frac{3}{2.5}} \text{ cals/sec.}$$

Heat taken by water $= m \times S \times \text{rise in temperature}$
 $= 100 \times 1000 \times 1 \times (\theta - 30) \text{ cals/sec.}$

$$\therefore \frac{2\pi \times 0.15 \times 200 \left(500 - \frac{30 + \theta}{2} \right)}{2.303 \log_{10} \frac{3}{2.5}} = 10^5 (\theta - 30)$$

$$\text{or } \theta = 34.9^{\circ}\text{C.}$$

$$\therefore \text{rise in temperature} = (\theta - 30) \\ = 34.9^{\circ} - 30 = 4.9^{\circ}\text{C}$$

Example 15. Water is pumped through an iron tube ($K = 0.16$), 2 metres long, at the rate of 1000 litres/minute the inner and outer diameters of the tube are 5 and 6 cms. respectively. Calculate the rise in temperature of the water when the outside of the tube is heated by a fire to 600°C , the initial temperature of water being 30°C . What would be the rise if a scale $\frac{1}{16}$ mm thick ($K = 0.004$) is formed on the inside surface of the tube. (A.M.I.E.)

Quantity of heat flowing in the cylindrical pipe.

$$Q = \frac{2\pi Kl(\theta_1 - \theta_2)}{2.303 \log_{10} \frac{r_2}{r_1}}$$

where $\theta_1 = 600^\circ\text{C}$ and $\theta_2 = \frac{30 + \theta}{2}$ θ being outlet temperature of the water.

$$= \frac{2\pi \times 0.16 \times 2 \times 100 \left(600 - \frac{30 + \theta}{2} \right) \times 60. \text{ cal/minute}}{2.303 \log_{10} \frac{3}{2.5}}$$

This is equal to the heat gained (taken) by water per minute

$$= m \times s \times \text{rise in temperature}$$

$$= 1000 \times 1000 \times 1 \times (\theta - 30) \text{ cal/min.}$$

$$= 10^6 (\theta - 30) \text{ cals/min.}$$

(ii)

Equating (i) and (ii) we have.

$$\theta = 66.3^\circ\text{C.}$$

$$\therefore \text{rise in temperature} = (\theta - 30) = 66.3^\circ - 30^\circ = 36.3^\circ\text{C}$$

When a scale of $\frac{1}{10}$ mm is formed inside the pipe then it becomes a case of two cylindrical layers in series and the expression for that the amount of heat conducted is given by

$$Q = \frac{2\pi l (\theta_1 - \theta_2)}{2.303 \left[\frac{1}{K_1} \log_{10} \frac{r_1''}{r_1'} + \frac{1}{K_2} \log_{10} \frac{r_2''}{r_2'} \right]}$$

Now

$$r_1'' = r_2' = 2.5 \text{ cm.}$$

$$r_1' = 2.5 - 0.01 \text{ cm.} = 2.49 \text{ cm.}$$

$$r_2'' = 3 \text{ cm.}$$

$$\therefore Q = \frac{2\pi \times 2 \times 100 \left(600 - \frac{30 + \theta}{2} \right)}{2.303 \left[\frac{1}{0.004} \log_{10} \frac{2.5}{2.49} + \frac{1}{0.16} \log_{10} \frac{3}{2.5} \right]} \times 60 \text{ cals/min.} \quad \dots(i)$$

Equating (i) and (ii),

$$\frac{2\pi \times 200 \left(600 - \frac{30 + \theta}{2} \right)}{2.303 \left[\frac{1}{0.004} \log_{10} \frac{2.5}{2.49} + \frac{1}{0.16} \log_{10} \frac{3}{2.5} \right]} \times 60 = 1000 \times 100 \times 1 (\theta - 30)$$

$$\therefore \theta = 30.76^\circ\text{C}$$

$$\therefore \text{rise in temperature} = \theta - 30 = 30.76 - 30 = 0.76^\circ\text{C}.$$

Example 16. A metal pipe having an external diameter 15 cm. carries steam at 200°C . This is covered by a layer 2.5 cm. thick of insulating material ($K=0.0005$). If the outer surface is at 100°C , calculate the heat loss per metre length per minute. Neglect temperature drop in the metal. Also calculate the amount of steam condensed per minute. (A. M. I. E.)

$$\begin{aligned} \text{Heat gained by the water flowing through the pipe} \\ = 1000 \times 1000 \times 1 \times (\theta - 30) \text{ cal/min.} \end{aligned}$$

$$\text{Now} \quad Q = \frac{2\pi l K (\theta_1 - \theta_2)}{2.303 \log_{10} \frac{r_2}{r_1}} \times 60 \text{ cals/min}$$

$$\text{Substituting } l = 1 \text{ metre} = 100 \text{ cms.}$$

$$r_1 = \frac{15}{2} = 7.5 \text{ cm.}$$

$$\begin{aligned} r_2 &= r_1 + \text{thickness of layer} \\ &= 7.5 + 2.5 = 10 \text{ cm.} \end{aligned}$$

$$\theta_1 = 200^\circ\text{C}$$

$$\theta_2 = 100^\circ\text{C}$$

and

$$K = 0.0005, \text{ we have}$$

$$\begin{aligned} Q &= \frac{2\pi \times 100 \times 0.0005 (200 - 100)}{2.303 \log_{10} \frac{10}{7.5}} \times 60 \\ &= 6580 \text{ cals/min.} \end{aligned}$$

$$\text{Amount of steam condensed } m = \frac{Q}{L}.$$

$$= \frac{\text{Heat lost by steam pipe}}{\text{Latent heat of steam}}$$

$$= \frac{6580}{540} = 12.2 \text{ gms/min.}$$

Example 17. Steam at 100°C passes through a rubber tube of inner and outer diameters of 1 cm. and 3 cm. respectively, the tube being immersed in ice. Find the temperature existing half way through the thickness of the wall of the tube. (A. M. I. E.)

Let θ be the temperature half way through the thickness of wall.

$$\therefore \quad r_1 = \frac{1}{2} = 0.5 \text{ cm.}$$

$$\text{and} \quad r_2 = 1.5 \text{ cm.}$$

$$\theta_1 = 100^\circ\text{C}$$

and

$$\theta_2 = 0^\circ\text{C}$$

$$\therefore Q = \frac{2\pi l K(\theta_1 - \theta_2)}{2.303 \log_{10} \frac{r_2}{r_1}} = \frac{2\pi l K(100 - 0)}{2.303 \log_{10} \frac{1.5}{0.5}} \quad \dots (i)$$

Now considering only half the thickness of the tube, then

$$r_1 = 0.5 \text{ cm.}$$

and $r_2 = 0.5 + \frac{1}{2} = 0.5 + 0.5 = 1 \text{ cm.}$

$$\theta_1 = 100^\circ\text{C}$$

and $\theta = \text{temperature half way through}$

$$Q = \frac{2\pi l K(100 - \theta)}{2.303 \log_{10} \frac{1}{0.5}} \quad \dots (ii)$$

Dividing (i) and (ii),

$$\frac{100 - \theta}{100 - \theta} = \frac{\log_{10} \frac{1}{0.5}}{\log_{10} \frac{1.5}{0.5}} = \frac{\log_{10} 2}{\log_{10} 3} = \frac{0.3010}{0.4771} = 0.631$$

$$\therefore 100 - \theta = 63.1$$

or $\theta = 100 - 63.1 = 36.9^\circ\text{C}$

11.10. Experimental determination of Conductivity. The following are the methods for determining the thermal conductivity for good conductors and the poor conductors of heat.

(i) **Searle's Method.** For good conductors like metal bars or rods.

(ii) **Lee's Method.** For good conductors like metal rods or bars. This method is quite suitable for the determination of the value of K at different temperatures.

(iii) **Cylindrical shell method.** For poor conductors like glass or rubber.

(iv) **Lee's disc method.** For poor conductors like rubber, glass, ebonite etc.

(i) **Searle's method.** The co-efficient of thermal conductivity of good conductors can readily be determined by means of **Searle's apparatus**, shown in Fig. 11.7. AB is a bar of the material whose co-efficient of conductivity is required. It is covered with some bad conductor e.g., felt or cotton to minimise heat losses from its surface. The end A is heated to steam temperature by placing it in a chamber through which steam is passed. Alternatively this end may be heated by an electric current. At the end B is wound a coil having

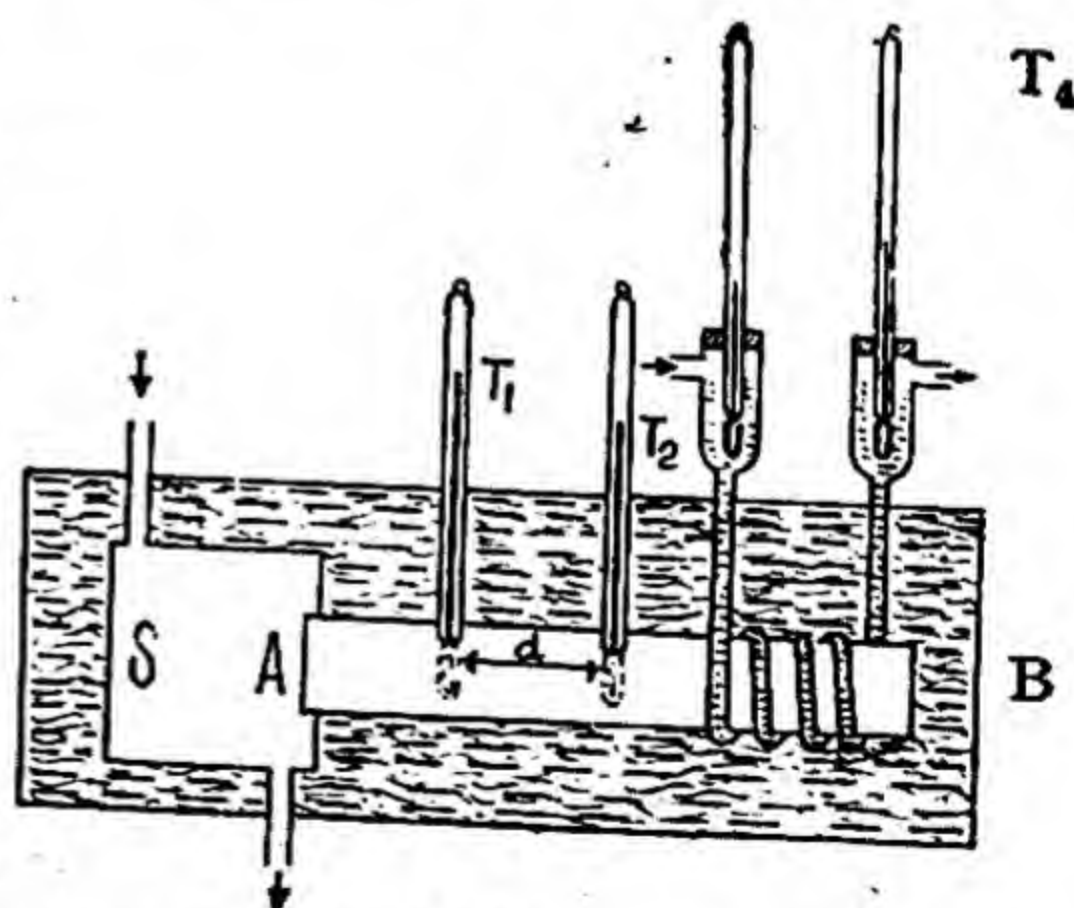


Fig. 11.7

two openings. Through this coil a steady flow of cold water is maintained. The temperature θ_3 and θ_4 of the water at the entrance and exit is noted by the two thermometers T_3 and T_4 placed in position as shown. Two other thermometers T_1 and T_2 are placed a known distance apart, in two cavities in the bar. To ensure good contact a little of mercury is placed in these cavities. *The flow of water is regulated in the coil so that a steady state of temperature is reached.* At this stage the quantity of heat flowing through any section of the bar is the same.

The quantity of water flowing through the coil, (when steady state has reached) in a given time, is collected and weighed. The temperature of the thermometers T_1 , T_2 , T_3 , and T_4 are also noted. Let m be the mass of this water which flows in the given time t and θ_3 and θ_4 be the temperatures of water at the entrance and exit respectively. Then, the heat which reaches the end B and is absorbed by water in t seconds,

$$= m(\theta_4 - \theta_3) \text{ cal.}$$

Let d be the length of the rod between the thermometers T_1 and T_2 and let θ_1 and θ_2 be the temperatures recorded by them. If A is the area of cross-section of the bar and K the co-efficient of thermal conductivity, then the amount of heat passing through these points in the given time t is,

$$= \frac{KA(\theta_2 - \theta_1)t}{d}$$

$$\therefore m(\theta_4 - \theta_3) = \frac{KA(\theta_2 - \theta_1)t}{d}$$

(ii) **Lee's method for good conductors.** This method is generally used to determine the conductivity of metals at various temperatures.

The material whose conductivity is required is taken in the form of a small rod. It is fitted in a copper frame M as shown in Fig. 11.8. A heating coil C_1 is provided at one end of the specimen and two platinum resistance thermometers T_1 and T_2 are placed near each of the ends at a known distance d apart. To adjust the temperature of the apparatus a heating coil C_2 is wound round the copper frame. The whole apparatus is kept inside a Dewar flask.

The apparatus is immersed in liquid air till the temperature falls below the temperature at which thermal conductivity is to be determined. The liquid air is poured out of the flask and the copper frame is heated by passing a current through the coil C_2 till the desired temperature is obtained.

The current is now passed through the coil C_1 and heating is continued till a steady

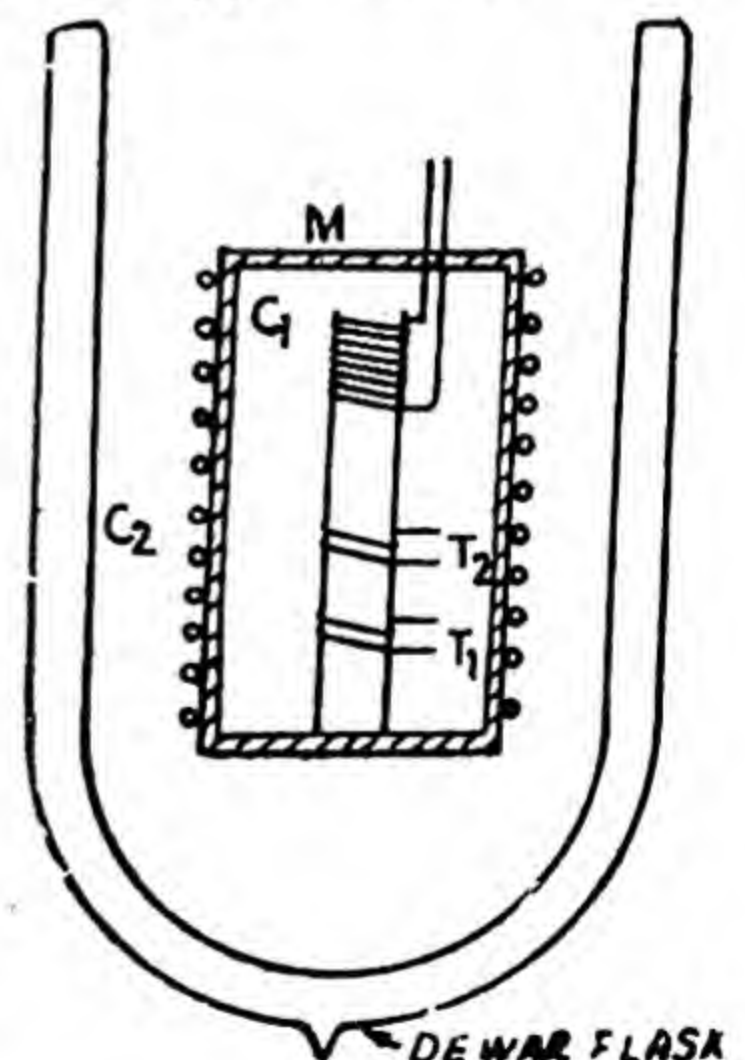


Fig. 11.8

state is reached *i.e.*, the thermometers T_1 and T_2 register a constant temperature difference $(\theta_2 - \theta_1)$.

If A is the area of cross-section of the rod and K its coefficient of thermal conductivity, then the quantity of heat passing in t seconds, is given by

$$Q = \frac{KA(\theta_2 - \theta_1)t}{d}$$

where d is the distance between the thermometers T_1 and T_2

Heat produced electrically = $\frac{EIt}{4.2}$ calories in t seconds, where E is the potential difference applied to the ends of the heating coil C_1 and I is the current in amperes.

Under steady conditions the two amounts of heat are equal

$$\begin{aligned} \text{Hence } \frac{EIt}{4.2} &= \frac{KA(\theta_2 - \theta_1)t}{d} \\ K &= \frac{EId}{4.2A(\theta_2 - \theta_1)} \end{aligned}$$

(iii) **Cylindrical Shell Method.** The apparatus for finding thermal conductivity K of glass in the form of a tube is shown in the Fig.11.9.

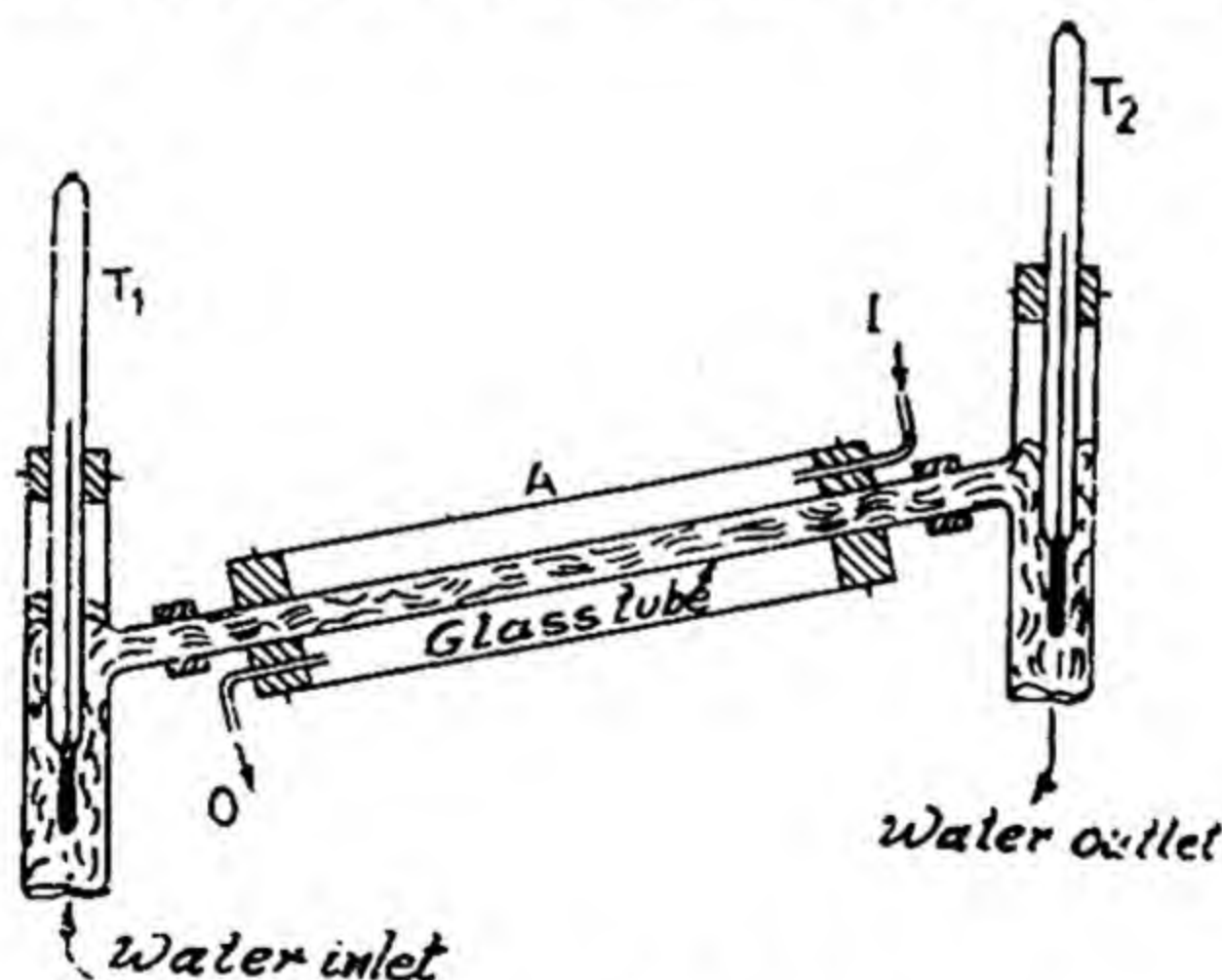


Fig. 11.9

It consists of a thick walled glass tube XY of length l , which is surrounded by steam by keeping it in a slanting position in the steam chamber A . A steady stream of water is allowed to pass through the tube at a uniform rate. This is achieved by placing a spiral wire along the axis of the glass tube. Steam is passed through the inlet I in the outer chamber A .

The water is heated by the heat given up by steam.

When steady conditions are reached, the heat passing through the walls of the tube is entirely taken up by water.

Two thermometers T_1 and T_2 are placed as shown, to record the temperatures of incoming and outgoing water.

When steady state has been reached, then

$$\text{Average temperature of water} = \frac{T_1 + T_2}{2} = \theta_2$$

and temperature of steam = θ_1

If m is the mass of water flowing per second, then

$$\text{Heat absorbed by water} \quad q = m (T_2 - T_1)$$

The inner and outer radii r_1 and r_2 of the glass tube are measured with the help of travelling microscope. Heat conducted through the cylindrical pipe is given by

$$q = \frac{2\pi l K (\theta_1 - \theta_2)}{2.3 \log_{10} \frac{r_2}{r_1}}$$

$$\text{But} \quad q = m (T_2 - T_1)$$

$$\therefore m (T_2 - T_1) = \frac{2\pi l K (\theta_1 - \theta_2)}{2.3 \log_{10} \frac{r_2}{r_1}}$$

$$\text{Hence} \quad K = \frac{m (T_2 - T_1) \cdot 2.3 \log_{10} \frac{r_2}{r_1}}{2\pi l (\theta_1 - \theta_2)}$$

Determination of the thermal conductivity of a rubber tube.

The thermal conductivity of a rubber tube can be found by first passing steam through it for a short time. The tube is then picked

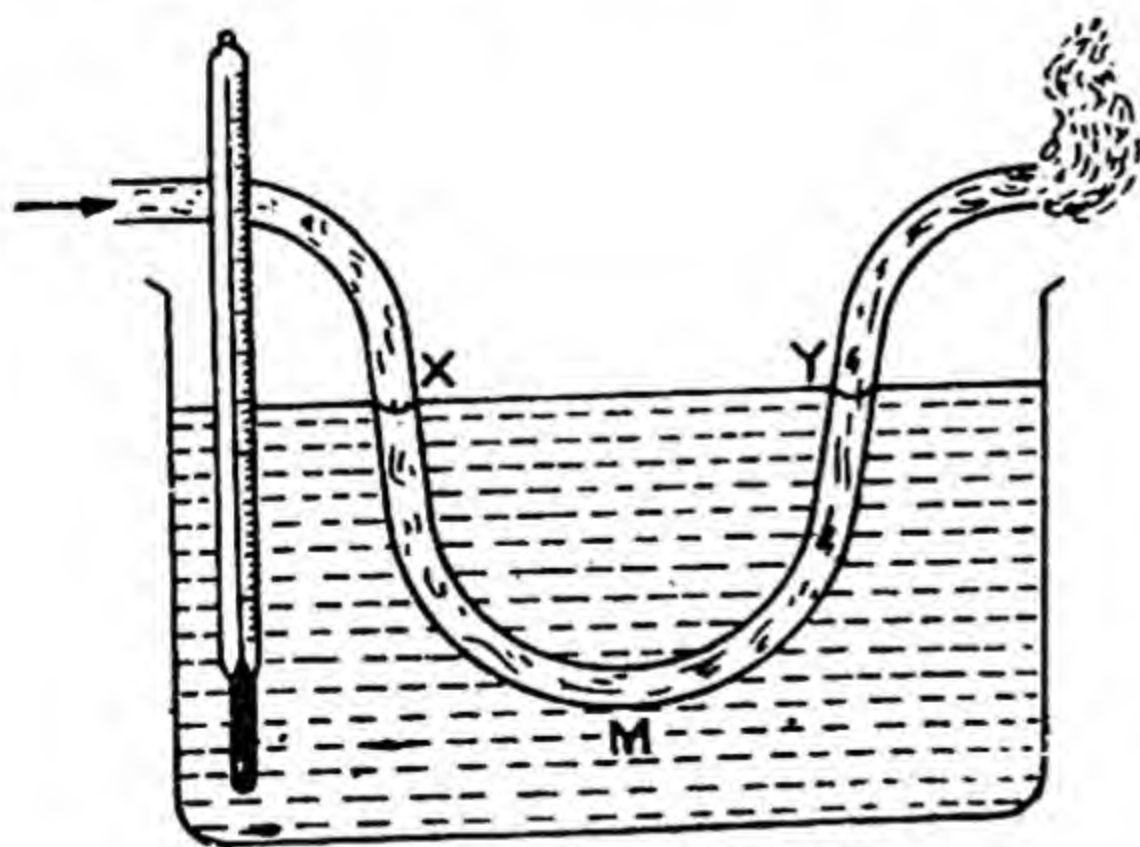


Fig. 11.10 (a)

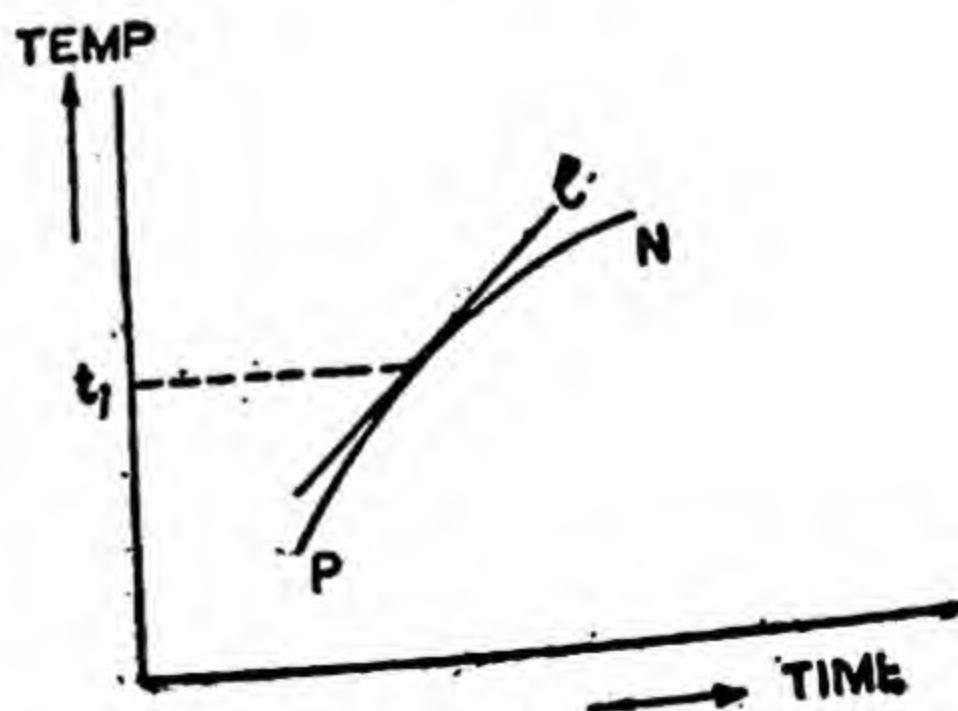


Fig. 11.10 (b)

up, with the steam still issuing from it, and a fixed length of it, XY , is immersed inside a calorimeter containing water, which has been

cooled several degrees below room temperature by addition of ice as shown in Fig. 11.10 (a). The temperature of water is then noted at equal intervals of time as it rises from initial temperature to a temperature N above the room temperature t_1 . From this graph the rise in temperature per sec, ($a^\circ\text{C}$ per sec. say) at the temperature θ_1 is obtained by drawing the corresponding tangent l to the curve.

When the water and calorimeter are at the same temperature as the room (t_1) no heat is lost by them to the surroundings. Thus the quantity of heat flowing per second (Q/sec) through the rubber tubing when immersed in the water is equal to the heat per second gained by water and calorimeter, at the temperature t ,

$$\text{Hence} \quad Q/\text{sec} = Wa \text{ cal/sec.}$$

$$\text{Where} \quad W = \text{total water equivalent of the water and calorimeter.}$$

$$\text{But} \quad Q/\text{sec} = KA \cdot \frac{d\theta}{dx}.$$

$$\therefore \quad Q/\text{sec} = K\pi (r_1 + r_2) l \frac{\theta - \theta_1}{r_2 - r_1}$$

$A = \pi (r_1 + r_2) l$ is the area through which heat is conducted and r_1 and r_2 are the internal and external radii of the tube and l is the length of XY .

$$\frac{d\theta}{dx} = \text{temperature gradient} = \frac{\theta - \theta_1}{r_2 - r_1}$$

$$\text{Thus} \quad Wa = K\pi (r_1 + r_2) l \frac{\theta - \theta_1}{r_2 - r_1}$$

The thermal conductivity K is calculated.

(iv) **Lee's method for bad conductors.** From the heat equation $q = \frac{KA(\theta_2 - \theta_1)}{x}$ it is clear that in the case of bad conductors like

card board or glass whose K is very small, q would also be small. In order to increase q , either temperature difference and A should be increased or thickness x should be decreased. As it is not possible to decrease x beyond a safe limit, q is increased by taking the material in the form of a **thin disc of large area**.

The apparatus as shown in Fig. 11.11 consists of two thin discs D_1 and D_2 of the material about 0.1 metre in diameter and about 2 m.m. in thickness placed between four copper discs C_1, C_2, C_3 and C_4 . A thin layer of glycerine is applied to the faces of D_1 and D_2 to ensure good thermal contact with the copper discs.

The copper discs C_2 and C_3 are fixed on the opposite faces of heating coil H . The heating coil consists of a resistance wire

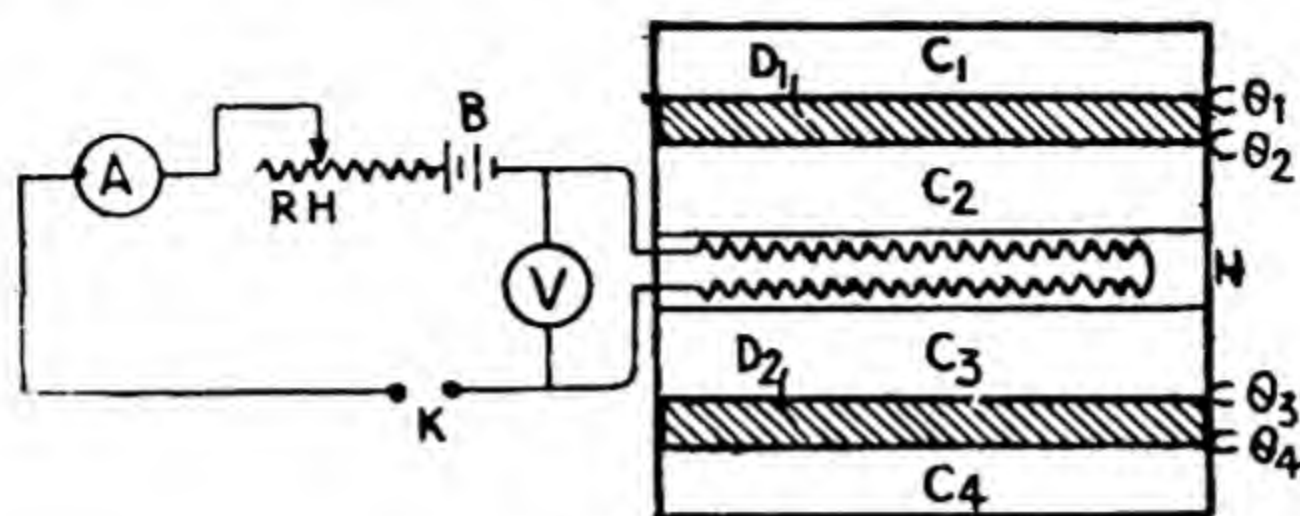


Fig. 11.11

wound on a mica strip as in an electric iron. It is heated by a battery from outside. The temperature at each face of the disc D_1 is noted by the thermocouples θ_1 and θ_2 and that at each face of the disc D_2 by thermocouple θ_3 and θ_4 . The whole apparatus is suspended inside a constant temperature enclosure.

A steady state current I amperes is passed through the heating coil and the potential difference E across it is measured. The heat so developed is conducted through C_1 and C_2 and then passes through D_1 and D_2 . The copper discs C_1 and C_2 are meant for ensuring uniform distribution of heat so that heat flow through D_1 and D_2 is normal and steady. When a steady state is reached the temperature of the thermocouples θ_1 , θ_2 , θ_3 and θ_4 are noted.

If the heat radiated from the edges of the discs C_2 , C_3 , D_1 and D_2 is neglected, then the quantity of heat produced by the heating coil H per second is equal to the quantity of heat passing per second through the discs D_1 and D_2 . This heat is radiated to the atmosphere by the copper discs C_1 and C_2 .

Let the thickness of the disc D_1 be x_1 and that of the disc D_2 be x_2 .

Area of each disc	$= A$
Thermal conductivity	$= K$
\therefore Heat passing per second across	$D_1 = \frac{KA (\theta_2 - \theta_1)}{x_1} \text{ cals.}$
" " " " "	$D_2 = \frac{KA (\theta_3 - \theta_4)}{x_2} \text{ cals.}$
Total heat conducted away	$= \frac{KA (\theta_2 - \theta_1)}{x_1} + \frac{KA (\theta_3 - \theta_4)}{x_2} \quad \dots (i)$

Heat produced per second electrically by the heating coil

$$Q = \frac{EI}{4.2} \text{ cals.} \quad \dots (ii)$$

Under steady conditions equations (i) and (ii) are equal and hence K can be calculated.

11.11 Convection. *It is that process of transmission of heat in which heat travels from one part of the body to another by the actual motion of heated particles of the medium.*

The process of convection can be demonstrated experimentally as given below.

(i) *Convection in liquids.* Drop a few tiny crystals of $KMnO_4$ near its side as shown. On heating the water a stream of colour will be seen rising from the bottom and then travelling in the direction marked by the arrows. This can be explained as follows.

Water at the bottom gets heated, expands, becomes lighter and rises up. Cold water from the top being heavier moves downwards and occupies the position of water that has gone up. Thus convection currents are set up.

Convection is possible only in liquids and gases because convection currents cannot be set up in solids. In fact, this is the only important method of heating liquids and gases. The existence of convection currents in gases can be shown by a simple experiment given below.

(ii) *Convection in gases.* Take a box fitted with two card board tubes P and Q . Place a candle with its flame under the

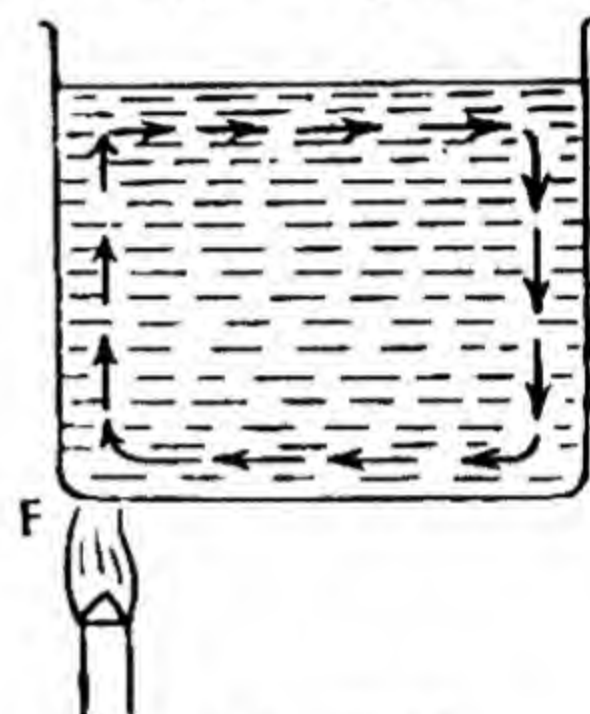


Fig. 11.12

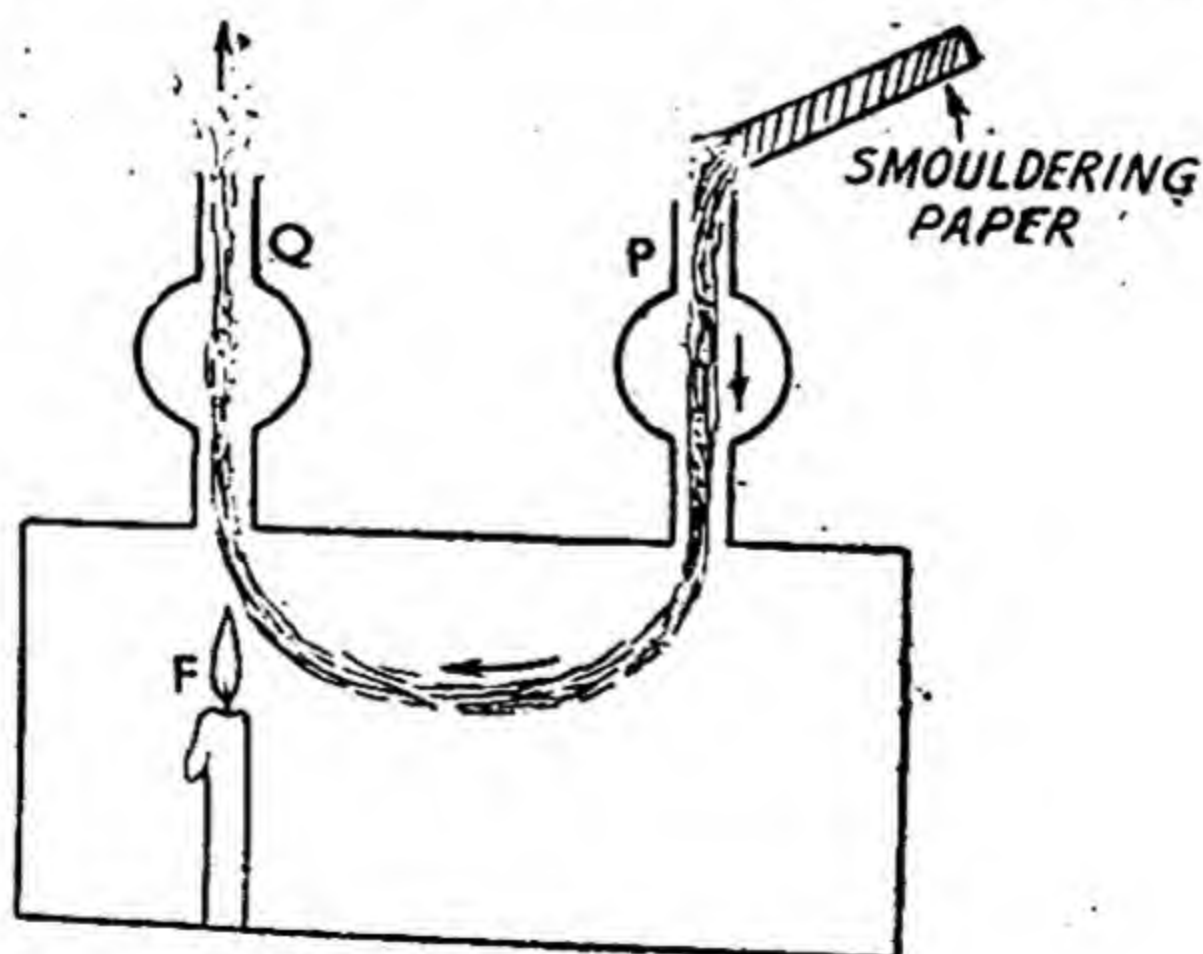


Fig. 11.13

tube Q . If a smouldering piece of brown paper is brought near the opening of the tube P , the smoke moves down in the tube P and rises up in the tube Q as shown in Fig. 11.13. The

basis of this phenomenon is the same as that of convection currents in water. The hot air in the tube Q being less dense rises up and is replaced by the cold air through the tube P . The movement of the smoke shows the direction of the air travel.

Applications. Some applications of convection in nature and in industry are given here under.

(1) *Natural applications of Convection.* (a) Trade winds are caused by convection. In hotter regions the earth's surface gives heat to layers of air in contact with it. These layers of air rise up and are replaced by cold air from colder regions.

(b) During the day time the cool sea breeze blows from the sea to the land and at night the breeze blows from the land to the sea. During the day the earth gets more quickly heated (because of low specific heat) than water and cold sea breeze replaces the hot air which rises up from earth. During night as the earth gets quickly cooled, the land breeze replaces the hot air from sea which rises upwards.

(c) Monsoons are also convection currents in air on large scale. In summer, the Indian plains are very hot and the hot air rises up. Moist air from Indian ocean flows towards the land and on getting cooled causes rain fall.

(2) *Industrial applications of Convection* (a) The ventilators near the ceiling provide an out let for damp hot air exhaled by the inmates of the room, while fresh air enters through the doors and windows. In cinema halls etc. exhaust fans fitted near the ceiling throw out the foul air while fresh air enters through the openings near the floor.

(b) The draught in the chimney of a furnace is also produced by convection currents. A chimney above the furnace convects away the hot air while fresh air enters the chimney from below the fire. The higher and narrower the chimney, the better it is.

(c) Heating of buildings by hot water in cold countries.

(d) *Radiators in automobiles.* The heated water from the cylinders of the engine flows up through slanting pipes to the radiator when it gets cooled by air currents and returns down to the cylinder jacket at the bottom.

(e) *Gas filled Electric lamps.* A little argon gas introduced in the glass bulb convects away the heat from the tungsten filament uniformly in the bulb which enables the filament to get heated to a higher temperature without any fear of melting and thus more light is emitted by the lamp.

11.12 Radiation. We have already seen that *conduction* and *convection* are processes in which heat is carried from one place to another by the movement of the substance concerned. The heat from the sun which reaches the earth, however passes through a considerable region in which there is little or no material substance and hence heat can pass through a **vacuum**. In this case we speak of the heat **radiated** by the

sun. **Radiation** is the name given to the transfer of heat when the medium takes no part in the transfer. The heat energy transmitted by this process is called the *radiant energy* or *heat radiation* or *thermal radiation*. Heat radiation resembles in many ways with light energy. The major difference between them is their wavelength. Thermal radiation is of lower wave length than light hence they are invisible to the eye. In general the properties of radiant heat are similar to those of light. Some of the properties are

- (i) Heat radiation travels through vacuum with the velocity of light (3×10^8 m/sec).
- (ii) Heat radiation like light travel in straight line.
- (iii) Heat radiation obeys the law of inverse squares like light.
- (iv) Heat radiation is refracted according to the same laws as light
- (v) Heat radiation is refracted like light.
- (vi) Heat radiation exhibits the phenomena of interference and diffraction.
- (vii) Heat radiation can also be polarised like light.

When heat radiations fall on a body, some are absorbed, some reflected and the rest are allowed to pass through it. Those bodies which allow heat radiations to pass through them are called **diathermanous**, whereas those which absorb heat radiations and are themselves heated are called **athermanous**. No material medium is perfectly diathermanous, air is only approximately so. Rocksalt and Sylvine are diathermanous to a large extent. Water, wood and other liquids and solids are mostly athermanous.

11.13. Black body. Regarding the affect of the nature of the surfaces, it has been found experimentally that different surfaces *all at the same temperature* emit radiant energy at different rates but there is a maximum rate that none of them exceeds. It has also been found that different surfaces absorb different fractions of the radiant energy incident upon them. The hypothetical body whose surface would absorb all the radiation incident upon it is called a **black body**. Thus a perfectly black body is one which absorbs totally all the radiation of any wavelength which fall on it. Since it neither reflects nor transmits any radiation it appears black whatever the colour of incident radiation may be. A surface coated with lamp-black or platinum black absorbs from 96% to 98% of the incident radiations and may be considered as perfectly black body for practical purposes. On the other hand when such a body is heated it emits radiations of all possible wave lengths. The radiation emitted by a black body is known as *black body radiation* or *full radiation* or *total radiation*.

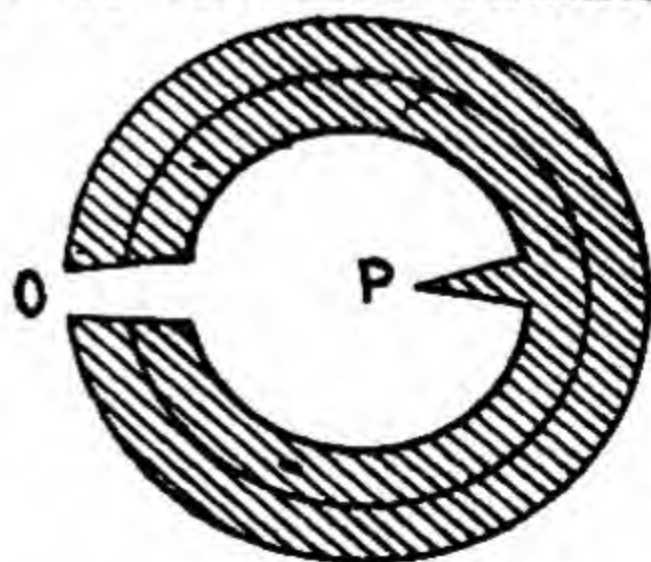


Fig. 11.14

Black body in practice. There is no such substance known which exactly behaves like a black body as described above. In practice, black body conditions can be closely realized by a small opening O in a closed chamber say a hollow sphere as shown in Fig. 11.14 maintained at a uniform temperature. If the radiation enters through the narrow opening O it is lost inside by successive reflections on the inner wall and whole of it is absorbed. Hence the opening behaves like a perfect absorber i.e., the opening or hole O (not the sphere) constitutes a black body. The type of black body shown in the figure was designed by **Ferry**. It is a closed hollow sphere painted black from inside having small opening O and a projection P opposite to the opening. This projection protects any direct reflection of the radiation into the opening O from the surface opposite to the hole.

If the enclosure is heated to a uniform high temperature, then the radiation coming out of the hole O are the full radiations or black body radiations.

11.14. Prevost's Theory of Exchanges. Before 1792 the ideas regarding radiant heat were very much confused. It was thought that the hot bodies were emitting hot radiations and the cold bodies were emitting cold radiations. Prevost was the first to recognise that this was incorrect.

He said that there was no such thing as cold radiation and proved that heat radiation was essentially an exchange process. *He said that all bodies at all temperatures (above absolute zero) were emitting radiant energy, the amount increased with the rise of temperature and was unaffected by the presence of the surrounding bodies. The rise or fall of temperature which is observed in a body is due to exchange of radiant energy with the surrounding bodies.* This is known as **Prevost's theory of exchanges**.

Near the fire we feel hot because our body receives more radiations than it gives out and near the block of ice, we feel cold because our body gives out more radiations than it receives. These considerations are quite general and may be applied to all similar phenomenon.

It is quite clear from the above facts that when a body absorbs more radiant energy (radiations) than what it emits, the body rises in temperature and when it absorbs less energy, it falls in temperature. When the quantity absorbed is equal to the quantity emitted the temperature of the body remains the same. When body has the same temperature as that of its surroundings it is a case of **dynamic equilibrium** that is at this stage the body gives out the same amount of heat radiations as it receives from the surroundings. As the temperature of surroundings rises or falls, the temperature of the body accordingly changes and the exchange of radiations continues. It only stops at absolute zero when all the molecular motion stops.

Hence it is concluded from the above explanation that the **absorbing power** of a surface is equal to the **emissive power**.

11.15. Absorbing and reflecting powers. When heat radiation falls upon a body, it is generally split into three parts :—

- (i) a part is **reflected** in accordance with the laws of reflection.
- (ii) a part is irregularly reflected or diffused at the surface and is thrown back in various directions and
- (iii) a part gets refracted into the body, of this, a portion may get transmitted through the body, while the remaining may be absorbed. The heat absorbed raises the temperature of the body.

The portion of heat absorbed or reflected depends upon the nature of the surface. Those which absorb more heat than what they reflect are called **good absorbers** while those surfaces which reflect more heat than what they absorb are called **good reflectors**.

Absorbing or absorptive power. *It is defined as the ratio of the amount of heat radiations absorbed by a body in the given time to the total amount of heat radiations incident on it in the same time. It is denoted by a_λ .*

If dQ is the amount of heat energy lying between wavelegths λ and $\lambda+d\lambda$ incident per unit area of the surface, then the amount of energy absorbed by it is equal to $a_\lambda dQ$. The rest of the energy which is equal to $(dQ - a_\lambda dQ)$ is either reflected or transmitted by it. Hence the absorptive power a_λ is defined as

$$a_\lambda = \frac{\text{Heat energy absorbed}}{\text{Heat energy incident}} = \frac{dQ_1}{dQ}$$

where $dQ_1 = a_\lambda dQ$

Reflecting power. If $dQ_2 = (dQ - a_\lambda dQ)$ is the portion of the incident radiations dQ which is reflected by a surface then the ratio $\frac{dQ_2}{dQ}$ is called reflecting power of the surface. Hence **reflecting power of a surface** is measured by the amount of heat radiations reflected by the surface to the amount of heat radiations incident on it in the given time.

The complete study of the above facts state that the heat radiation incident on the surface of a body from any source outside the body is partly absorbed and converted into heat, partly reflected, and may be partly transmitted through the body. The fractions accounted for in each of these ways vary widely for different materials. For example, both **asbestos paper** and **polished copper** transmit practically none of the radiant energy incident upon them. But asbestos paper absorbs almost all of it and reflects very little, whereas polished copper absorbs very little and reflects almost all. The fractions absorbed, reflected, and transmitted vary also with the wavelength of the incident radiation. For example, glass transmits almost all the incident radiations of the shorter wave lengths but transmit very little radiation of the longer wave lengths.

From the definitions of the above items like absorptive power and reflecting power it is clear that those substances which reflect more of incident radiations absorb less. Thus we see that good absorbers are bad reflectors. Dull black surfaces are bad reflectors and good absorbers whereas polished white surfaces are good reflectors and bad absorbers.

The absorbing power of a perfectly black body is unity as it absorbs all the radiations incident on it. Its reflecting power is zero.

Emissivity of a surface is defined as the amount of heat radiated per second by a unit area of the surface when the difference of temperature between the body and its surroundings is 1°C .

The amount of heat radiated per second by a surface depends upon the following factors.

- (i) Area of the surface A
- (ii) Difference of temperature between the surface and its surroundings θ
- (iii) Nature of the surface.

$$\therefore Q \propto A \times \theta$$

$$\text{or } Q = A \theta \times e$$

where e is the emissivity.

The emissive power or radiating power of a surface is defined as the ratio of the amount of radiations emitted by unit area of the surface to the amount emitted per second by unit area of a perfectly black body, the emissions taking place under identical conditions. The emissive power of a perfectly black body is regarded as unity. If we confine ourselves to the radiant energy emitted between the wavelength λ and $\lambda + d\lambda$ then in the limit $d\lambda \rightarrow 0$, we may write e_λ for the emissive power of the body for radiation of wave length λ .

We must be careful not to confuse *emissive power* as defined above with *emissivity*.

In the first instance the various properties of a substance relating to radiation were defined in a *relative* manner. An exact definition of emissive power is given below.

The emissive power e_λ of a body at a temperature T° for wavelength λ is defined as the energy radiated into vacuum per second per sq. cm. per unit range of wave length. The energy radiated per second per unit area lying between the wave lengths λ and $(\lambda + d\lambda)$ is then given by $e_\lambda d\lambda$. The emissive power of a perfectly black body is maximum and is denoted by E_λ .

The **absorptivity** a of a surface for radiation of any wave length is the fraction of the incident radiation of the given wave length that the surface absorbs.

Grey surface. A gray surface is defined as one whose emissivity is the same at all wave lengths and temperatures. Hence the ratio of the rate at which a grey surface emits radiation of any wave length to the rate at which a black body at the same temperature would emit radiation of the given wave length is constant for all wave lengths. Therefore for a grey surface.

$$e = \frac{\text{The total rate at which grey surface emits radiation of all wave lengths}}{\text{The total rate at which a black body at the same temperature would emit radiation of all wave lengths}}$$

None of the surfaces found in the engineering practice is actually grey but the error introduced by assuming them to be such is usually small.

11.16 Laws of Black Body Radiations. The Laws of heat radiations are

- (i) Wien's Law.
- (ii) Kirchoff's Law.
- (iii) Stefan's Law.

(i) **Wien's Law.** It is a common phenomenon that the colour of light emitted by a hot body changes as the temperature of the body rises, first glowing to a red then orange and finally white. The wave length decrease progressively as we go through these stages of various colours. Thus we see that the quantity of energy radiated is not uniformly distributed over all wave lengths but is maximum at one wave length say λ_m depending on the absolute temperature T of the black body. With the increase in temperature the value of wave length which carries maximum energy is decreased. In other words, wave length corresponding to the maximum energy is inversely proportional to the absolute temperature of the body.

$$\therefore \lambda_m T = \text{constant}$$

[The value of the constant = 0.2898 cm deg].

This is known as **Wien's Law**. It states that the wave length corresponding to the maximum energy is inversely proportional to the absolute temperature. The curves in fig. 11.15, show how the radiant energy in different wave lengths E_λ varies with the wave length λ for different temperatures of the black body radiator. At a given temperature 1650°K for example, there is very little radiant energy E_λ in the visible spectrum but the energy increases to maximum as longer wave lengths are reached and then decreases to zero. It will be seen from the curves that for each temperature there is a wave length λ_m for which the energy in the spectrum is maximum and that the value of λ_m decreases with the rise in temperature which is in accordance with

Wien's Law.

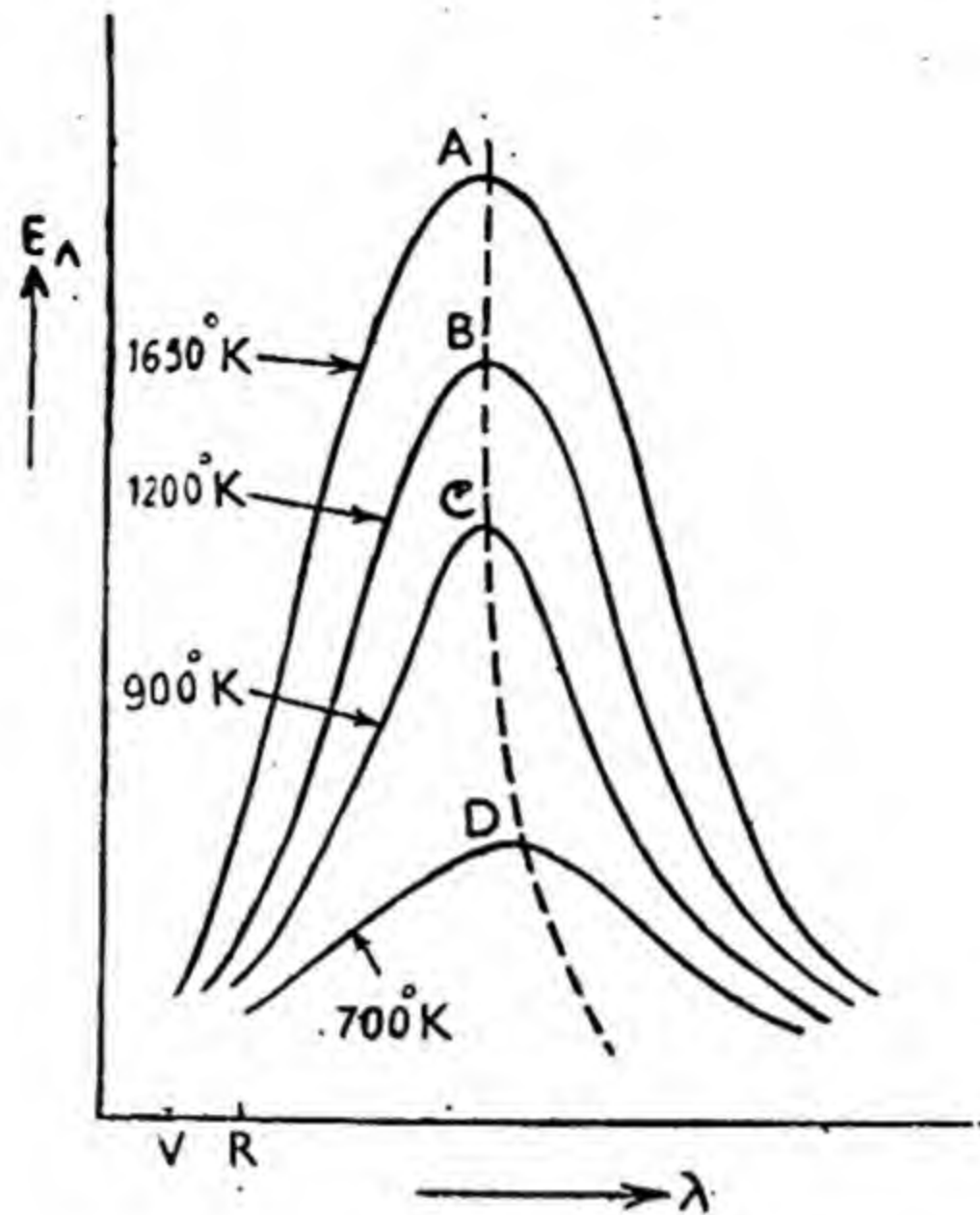


Fig. 11.15.

(ii) **Kirchoff's Law.** From a consideration of the emissive and absorptive powers of various substances it was observed that those substances which have a high value for the absorptive power have a high value for the emissive power. The relation pointed out between absorptive power and emissive power is embodied in a law known as **Kirchoff's Law**. Thus Kirchoff's Law states that at a given temperature the ratio of the emissive power to the absorptive power for radiations of a given wavelength is a constant for all bodies and is equal to the emissive power of a perfectly black body.

To prove the above statement. Consider an enclosure whose walls are maintained at a uniform temperature as shown in the Fig. 11.16. Let a body A of emissive power e_λ and absorptive power a_λ be placed in the enclosure, irrespective of the initial temperature of the body A , an exchange of heat will take place between the body and the surrounding enclosure and after some time a state of thermal

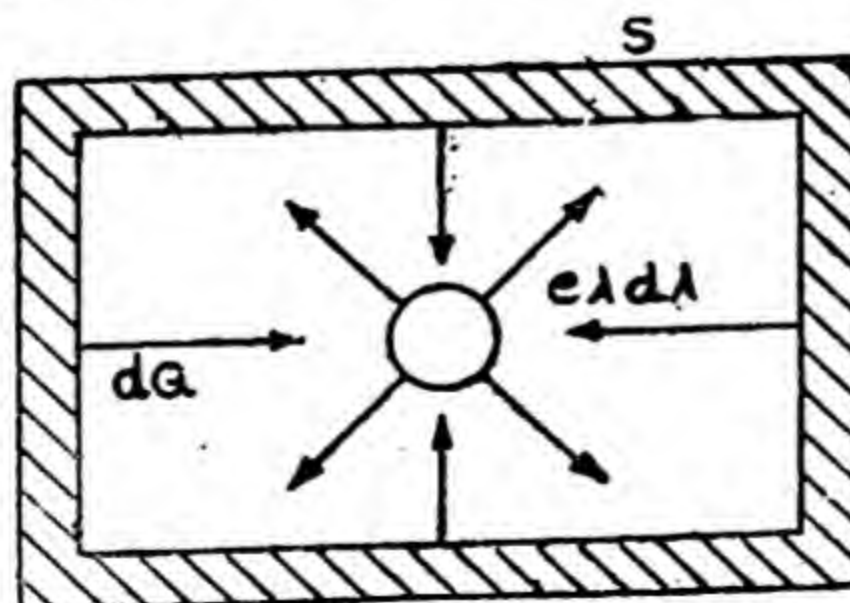


Fig. 11.16

equilibrium will be established between the two.

Let dQ be the quantity of energy between the limiting wavelength λ and $\lambda + d\lambda$ received in one second on a unit area of surface by this body.

The body A will absorb a certain fraction a_λ of this energy that is, an amount $a_\lambda dQ$, where a_λ is the absorptive power of A for a wavelength λ . The remainder of this energy $(1 - a_\lambda) dQ$, will be reflected or transmitted.

Let e_λ be the emissive power of A for radiation of wavelength λ , and let E_λ be the emissive power of a perfectly black body under the same conditions.

The energy emitted in one second by unit surface of A by virtue of its temperature is $e_\lambda d\lambda$,

The total energy given out in one second by unit surface of $A = (1 - a_\lambda) dQ + e_\lambda d\lambda$... (i)

This must be equal to the energy received dQ , when a state of equilibrium is received.

$$\therefore (1 - a_\lambda) dQ + e_\lambda d\lambda = dQ \quad \dots (ii)$$

In the case of a black body, the emissive power is E_λ and the absorptive power is unity

$$\therefore E_\lambda d\lambda = dQ \quad \dots (iii)$$

Substituting this value of dQ in equation (ii), we have

$$(1 - a_\lambda) E_\lambda d\lambda + e_\lambda d\lambda = E_\lambda d\lambda$$

$$\therefore e_\lambda = a_\lambda E_\lambda,$$

$$\text{or} \quad \frac{e_\lambda}{a_\lambda} = E_\lambda = \text{constant for all substances} \quad \dots (iv)$$

Which is Kirchhoff's Law. It is clear from the expression that if e_λ is large then a_λ should also be correspondingly large which means good radiators are good absorbers.

Applications of Kirchhoff's Law.

(a) If a piece of china clay which possesses some colouring material in portions of its surface is heated in a furnace and is then taken to a dark room, the coloured pattern will shine out more brightly than the white background. This is because the coloured surface is a better absorber than the white background, and in consequence also emits a greater quantity of light.

(b) The sodium vapour when hot emits the two yellow lines called D_1 and D_2 but when cold absorbs these very lines. This shows that a substance which is a good emitter of certain wavelength is also good absorber of the same wavelength.

(iii) **Stefen's Law.** It states that the total radiation E from a black body per second per unit area is directly proportional to the fourth

power of the absolute temperature T i.e.,

$$E \propto T^4 \quad \text{or} \quad E = \sigma T^4$$

Where σ is a constant known as Stefan's constant.

The value of $\sigma = 5.735 \times 10^5$ ergs/cm²/sec/K⁴ (ergs cm⁻² sec⁻¹ K⁻⁴) in the C.G.S. system of units

and $\sigma = 5.735 \times 10^{-8}$ joules/m²/sec/K⁴
(Joules m⁻² sec⁻¹ K⁻⁴) in M.K-S. system of units
 $= 5.735 \times 10^{-8}$ watts/m²/K⁴ (watts m⁻² K⁻⁴)

because 1 joule/sec = 1 watt

As applied to a grey body having an emissivity of e , the above law becomes

$$E = \sigma e T^4$$

Suppose a black body at T_1 is surrounded by another black body at T_2 , then

Rate of energy emitted by first black body per sq. cm. at

$$T_1^\circ \text{K} = \sigma T_1^4$$

Rate of energy emitted by the second black body per sq. cm.

$$\text{at } T_2^\circ \text{K} = \sigma T_2^4$$

Hence, the net rate of loss or gain of energy radiation per unit time per unit area

$$E_{\text{net}} = \sigma(T_1^4 - T_2^4)$$

But the law can be extended to represent the net loss of heat by a body after exchange with the surroundings and enunciated as follows.

If a black body at absolute temperature T_1 is surrounded by another black body at absolute temperature T_2 , the amount of heat lost by the former per sec per sq. cm. is given by

$$E = \lambda(T_1^4 - T_2^4)$$

Thus statement goes in support of Prevost's theory of heat exchanges, that the observed loss of heat is really the difference in the heat radiated by the hot body and that absorbed by it from its surroundings.

Boltzman in 1884 gave theoretical proof of the Stefan's Law based on the thermodynamical considerations. Hence the Stefan's Law is also goes by the name *Stefan Boltzman's Law* and σ is called the Stefan Boltzman's constant. Boltzman showed that the law is strictly applicable to all black body radiations.

11.17. Newton's Law deduced from Stefan's Law. Considering a hot body at absolute temperature T_1 placed in an enclosure at absolute temperature T_2 , the rate of loss of heat according to Stefan's Law is given by

$$\begin{aligned} E &= \sigma(T_1^4 - T_2^4) \\ &= \sigma(T_1^2 - T_2^2)(T_1^2 + T_2^2) \\ &= \sigma(T_1 - T_2)(T_1 + T_2)(T_1^2 + T_2^2) \\ &= \sigma(T_1 - T_2)(T_1^3 + T_1^2 T_2 + T_1 T_2^2 + T_2^3) \end{aligned}$$

If the temperature difference $(T_1 - T_2)$ is small i.e., T_1 is nearly equal to T_2 , the above expression can be approximately written as,

$$E = \sigma(T_1 - T_2) \times 4T_2^3 \\ = k(T_1 - T_2)$$

if the enclosure is maintained at constant temperature T_2 , where $k = 4\sigma T_2^3$ (a constant).

This shows that the rate of loss of heat is proportional to the excess of temperature, provided the difference of temperature is small, which is **Newton's Law of Cooling**.

Example 1. Calculate the maximum amount of heat which may be lost per sec. by radiation from a sphere of 10 cms diameter at a temperature of 227°C when placed in an enclosure at a temperature of 27°C . Given that $\sigma = 5.7 \times 10^{-12}$ watts/cm²/K⁴.

According to Stefan's Law, energy radiated per sec. per sq. cm is given,

$$E = \sigma(T_1^4 - T_2^4) \text{ ergs}$$

$$\text{Total surface area of the sphere} = 4\pi r^2 = 4 \times 3.14 \times 5^2$$

$$\therefore \text{Net rate of loss of energy} = E \times 4\pi r^2 \text{ ergs/sec}$$

$$\therefore \text{Heat lost/sec} = \frac{\sigma(T_1^4 - T_2^4)}{J} \times 4\pi r^2 \text{ cal/sec.}$$

where J is the mechanical equivalent of heat $= 4.2 \times 10^7$ ergs/cal

$$\text{Now } \sigma = 5.7 \times 10^{-12} \text{ watts/cm}^2/\text{K}^4$$

$$\text{or } \sigma = 5.7 \times 10^{-5} \text{ ergs/cm}^2/\text{K}^4$$

$$T_1 = 227 + 273 = 500^\circ\text{K}$$

$$T_2 = 27 + 273 = 300^\circ\text{K.}$$

$$\therefore \text{Rate of heat lost/sec} = \frac{5.7 \times 10^{-5} \times (500^4 - 300^4) \times 4 \times 3.14 \times 25}{4.2 \times 10^7} \\ = 23.4 \text{ cal/sec.}$$

Example 2. A black body with an initial temperature of 300°C is allowed to cool inside an evacuated enclosure surrounded by melting ice at the rate of 0.35° per sec. If the mass, specific heat and surface area of the body are 32 gm., 0.1 and 8 sq. cm. respectively, calculate Stefan's constant.

According to Stefan's Law the energy radiated/sec/unit area is given by $\sigma(T_1^4 - T_2^4)$ ergs/sec/cm².

If A is the surface area of body, then total energy lost per sec. is given by,

$$E = A\sigma(T_1^4 - T_2^4) \text{ ergs/sec.}$$

$$= \frac{A\sigma(T_1^4 - T_2^4)}{J} \text{ cal/sec.} \quad \dots(i)$$

Now heat lost/sec. from the body

$$E = mS \times \text{rate of fall of temperature}$$

$$= 32 \times 0.1 \times 0.35 = 1.12 \text{ cal/sec.} \quad \dots(ii)$$

Equating (i) and (ii) we have

$$1.12 = \frac{A\sigma(T_1^4 - T_2^4)}{J}$$

Now

$$A = 8 \text{ sq. cm.}$$

$$T_1 = 273 + 300 = 573^\circ K$$

$$T_2 = 0 + 273 = 273^\circ K$$

\therefore

$$\sigma = \frac{J \times 1.12}{A(T_1^4 - T_2^4)} = \frac{4.2 \times 10^7 \times 1.12}{8(573^4 - 273^4)}$$

$$= 5.735 \times 10^5 \text{ ergs/sec/cm}^2/\text{K}^4.$$

Example 3. A black body is placed in an evacuated enclosure whose walls are blackened and kept at $27^\circ C$. Compare the net amount of heat gained or lost by the body (i) when its temperature is $227^\circ C$ and (ii) when its temperature is $-73^\circ C$.

According to Stefan's Law of radiation, radiation energy emitted or gained by a body is proportional to T^4 .

or $E = \sigma T^4$ where σ is Stefan's constant.

\therefore Heat lost by the black body per sec. per sq. cm. of its surface at $227^\circ C$ or $500^\circ K$

$$= \sigma(500)^4.$$

\therefore Heat gained by the black body per sec per sq cm. from the walls of enclosure at $27^\circ C$ or $300^\circ K = \sigma(300)^4$.

Net heat energy lost/sec/sq cm of the black body is

$$E_{net} = \sigma[(500)^4 - (300)^4] = 544 \times (100)^4 \times \sigma$$

$$= 544 \times 10^8 \times \sigma$$

(ii) Heat emitted by black body when at $(-73^\circ C)$ or $200^\circ K$

$$= \sigma(200)^4$$

Heat absorbed by black body from the walls is

$$= \sigma(300)^4.$$

\therefore Net heat energy gained by it from the enclosure walls

$$= \sigma[(300)^4 - (200)^4] = \sigma \times 65 \times 10^8$$

\therefore Ratio of heat energy lost at $227^\circ C$ to the heat energy gained at $73^\circ C$.

$$= \frac{544 \times 10^8 \times \sigma}{65 \times 10^8 \times \sigma}$$

$$= 544 : 65$$

$$= 41.85 : 5$$

or

Example 4. Luminosity of Rigal star in orion consellation is 17000 times that of our sun. If the surface temperature of the sun is $6000^\circ K$, calculate the tempereture of the star.

THERMAL CONDUCTIVITY

Taking the sun and the star to be perfect black bodies. let $T^\circ K$ be the temperature of the star.

Temperature of the sun $= 6000^\circ K$

Heat radiated by the sun per sec. per unit area $= \sigma (6000)^4$

Heat radiated by the star per second per unit area $= \sigma T^4$

Since luminosity of the star is 17000 times that of the sun

$$\therefore \sigma T^4 = 17000 \times \sigma (6000)^4$$

$$\therefore T = 6000 (17000)^{\frac{1}{4}}$$

$$= 68520^\circ K$$

Example 5. Calculate the surface temperature of the sun and moon ; given that $\lambda_m = 4573$ A.U. and 14μ respectively, λ_m being the wave length of the maximum intensity of emission. (A.M.I.E.)

According to Wien's displacement law,

$$\lambda_m T = \text{constant} = 0.2898$$

(i) For Sun.

$$\lambda_m = 4573 \times 10^{-8} \text{ cm. (1 A.U.} = 10^{-8} \text{ cm.)}$$

$$\therefore \lambda_m T = 0.2898$$

$$\text{or } T = \frac{0.2898}{4573 \times 10^{-8}} = 6097^\circ K$$

(ii) For Moon.

$$\lambda_m = 14 \mu = 14 \text{ micron}$$

$$[1 \text{ micron} = 10^{-3} \text{ m.m.} = 10^{-4} \text{ cm.}]$$

$$\therefore 14 \mu = 14 \times 10^{-4} \text{ cm.}$$

$$\therefore T = \frac{0.2898}{\lambda_m} = \frac{0.2898}{14 \times 10^{-4}} = 207^\circ K.$$

Example 6. Two bodies P and Q are kept in evacuated vessels maintained at a temperature of $27^\circ C$. The temperature of P is $327^\circ C$ and that of Q is $127^\circ C$. Compare the rate at which heat is lost from P and Q.

For the body P

$$T = 327^\circ C = 600^\circ K$$

$$T_o = 27^\circ C = 300^\circ K$$

We know

$$E = \sigma (T^4 - T_o^4)$$

\therefore

$$E_p = \sigma (600^4 - 300^4)$$

...(i)

For the body Q

$$T = 127^\circ\text{C} = 400^\circ\text{K}$$

$$T_q = 27^\circ\text{C} = 300^\circ\text{K}$$

$$E_q = \sigma [T^4 - T_o^4] = \sigma (400^4 - 300^4) \quad \dots (ii)$$

Dividing (i) by (ii), we have

$$\frac{E_p}{E_q} = \frac{\sigma (600^4 - 300^4)}{\sigma (400^4 - 300^4)} = \frac{100^4 (6^4 - 3^4)}{100^4 (4^4 - 3^4)}$$

$$= \frac{1296 - 81}{256 - 81} = \frac{1215}{175} = 6.95.$$

Example 7. Suppose that the maximum temperature in an atomic bomb explosion is 10^7°K . What is the corresponding wave length of maximum energy?

According to wien's law $\lambda_m T = \text{constant} = 0.2898$

$$\therefore \lambda_m = \frac{0.2898}{T} = \frac{0.2898}{10^7}$$

$$= 2.9 \times 10^{-8} \text{ cm},$$

or

$$\lambda_m = 2.9^\circ\text{A.U.}$$

Expected questions

1. (a) Define (i) Thermal conductivity and (ii) Thermal resistance. What are their units in C.G.S. and M.K.S. systems. Find the dimensions of conductivity.

(b) Describe with experimental details Searle's apparatus for determining the conductivity of metals. State the various sources of error and indicate other methods by which they are taken care of.

2. Derive an expression for the rate of flow of heat through thick metallic tubes.

3. Describe Lee's method for the determination of thermal conductivity of (i) metals and (ii) poor conductors.

4. What do you understand by diffusivity? How does it differ from thermal conductivity?

5. Describe and explain the cylindrical shell method of determining conductivity of a solid. Derive the formula used.

6. (a) How do you define the emissive and absorptive powers of a body?

(b) Name the three principal laws governing the heat radiations from black body?

(c) What is Stefan's Law and Stefan's constant. Give the value of Stefan's constant in C.G.S. and M.K.S. system of units.

7. (a) Explain the Prevost's theory of exchanges.

(b) Explain Kirchoff's law and give a few applications of this Law.

CHAPTER XII

THERMOMETRY

12.1. General. The degree of hotness of a body is known as its temperature. The science of measuring temperature is known as, **Thermometry**. In order to secure a reliable method of temperature measurement, some property of matter is chosen which varies continuously with temperature. Solids, liquids and gases all expand when heated, hence the amount of expansion or contraction of a material can be taken as an index of temperature. Mostly the property of expansion is utilised in the thermometers.

(a) (i) Thus a liquid enclosed in a glass tube of extremely fine bore is a very practical form of instrument for measurement of temperature. The *alcohol* and the *mercury* thermometers fall in this category and are very widely used.

(ii) A gas can also be used, but the apparatus required to measure the expansion of a gas makes the method unsuitable for industrial use, and its application is better limited to temperature measurement in the laboratory. *Constant Volume hydrogen thermometer* belongs to this type.

(b) The electrical resistance of metals increases when the temperature of the metal increases. Hence the change of resistance of a metal may be taken as a measure of its change of temperature. The *platinum resistance thermometers* fall under this category.

(c) If two wires of dissimilar metals be joined at their ends and the temperature of one junction be raised above that of the other, an electric current will flow through the circuit, and the potential difference between the two junctions may be used as a measure of the temperature difference between them. This is a Seebeck effect, and the working of *thermoelectric thermometers* or *thermo-couples* depend upon this principle.

It should be noticed that all these instruments indicate the temperature of the material constituting the thermometer, and therefore precautions should be taken to ensure that the material has acquired the temperature of the solid, liquid or gas whose temperature is being measured.

Fixed points. At least two points of reference must be arbitrarily selected or agreed upon, and the interval between these two points can then be arbitrarily subdivided to give any desired scale of temperature.

It is essential that the two points of reference should be such as can be easily reproduced with great accuracy. For example, the temperature at which a pure solid melts in the atmosphere is but very little affected by small changes in atmospheric pressure. This temperature can therefore be used as a point of reference. Any solid can be chosen, an obvious choice is ice and the temperature at which pure ice melts has been called the **lower fixed point**.

Lower fixed point is the melting point of ice. The second or *upper fixed point* may be the temperature at which a liquid boils, and here again water is the obvious liquid to choose.

Upper fixed point is the temperature at which pure water boils at normal atmospheric pressure i.e. at 760 mm of Hg.

The difference between these two fixed points is called as **Fundamental Interval**.

12.2. Scale of Temperature. For the purpose of practical measurements, a temperature scale based on a number of fixed points that can be reproduced with a high degree of accuracy has been adopted. There are following types of temperature scales.

(i) **Centigrade or Celsius Scale ($^{\circ}\text{C}$).** This thermometric scale was suggested by the Swedish Astronomer Celsius and is, therefore, called the Celsius Scale. It is based on the freezing point of water taken as zero degree and boiling point of water 100° both under standard pressure. This scale is used in scientific work.

(ii) **Fahrenheit Scale ($^{\circ}\text{F}$).** It is a thermometric scale devised by Fahrenheit on which freezing point of water is taken as 32° and boiling point of water as 212° both under standard pressure. It is used in engineering, medicine, and meteorology.

(iii) **Reaumur Scale ($^{\circ}\text{R}$).** It is a thermometric scale in which freezing point of water corresponds to 0° and the boiling point of water under normal pressure is taken as 80° . This scale is used for medical and domestic purposes in several European Countries.

(iv) **Kelvin Scale ($^{\circ}\text{K}$).** The absolute scale ($^{\circ}\text{A}$) is also called as Kelvin Scale. ($^{\circ}\text{K}$). On this scale.

$$\therefore 0^{\circ}\text{C} = 273^{\circ}\text{K} \text{ or } 273^{\circ}\text{A}.$$

$$T^{\circ}\text{K} = t^{\circ}\text{C} + (273)$$

This is used in scientific calculations.

(v) **Rankine Scale ($^{\circ}R_n$).** It is the temperature scale which corresponds to Kelvin scale but is based on the absolute zero of the Fahrenheit System. Thus

$$0^{\circ} \text{ Rankine} = -460^{\circ} F$$

$$T^{\circ} K = (t^{\circ} F + 460)$$

Relationship between Various Scales. The following equations give the relation between various scales.

$$\frac{C}{100} = \frac{F - 32}{180} = \frac{R}{80}.$$

In this way it is possible to convert a temperature reading from one scale to another.

Also

$$C = \frac{5}{9} (F - 32) = K - 273$$

$$= \frac{5}{9} R_n - 460$$

Where

C = temperature in $^{\circ}C$
 F = temperature in $^{\circ}F$
 R = temperature in $^{\circ}\text{Reaumur}$
 K = temperature in $^{\circ}\text{Kelvin}$
 R_n = temperature in $^{\circ}\text{Rankine}.$

12.3. Liquid Thermometers. Liquid thermometers are generally known as liquid in glass thermometers and commonly used liquids are mercury and alcohol. We will discuss only two types viz :—

- (i) Mercury in glass thermometer.
- (ii) Alcohol thermometers.

(i) **Mercury in glass Thermometer.** It consists of a fine bore glass capillary tube with a bulb blown at one end. The bore is made as uniform as possible. The bulb and the stem of the thermometer are filled with mercury by the method of alternate heating and cooling. The bulb is then kept in boiling water for some time to expel traces of air and moisture. The open end is finally hermetically sealed.

By placing the thermometer in pure melting ice, the lower fixed point can be marked on the tube. Similarly, by placing the thermometer in steam, the upper fixed point can be marked. The interval between the lower fixed point and the upper fixed point is known as fundamental interval and is divided into a number of equal parts each called a degree which indicates temperature. The number of degrees depend upon the scale chosen.

On the *Centigrade scale* the interval is divided into 100 equal parts the lower fixed point is given the value of 0° and the upper fixed point 100° .

On Fahrenheit, scale, the interval is divided into 180 equal parts the lower fixed point is given the value 32° and the upper fixed point 212° .

Similarly on the Reaumur scale, the interval is divided into 80 equal parts from 0° to 80° .

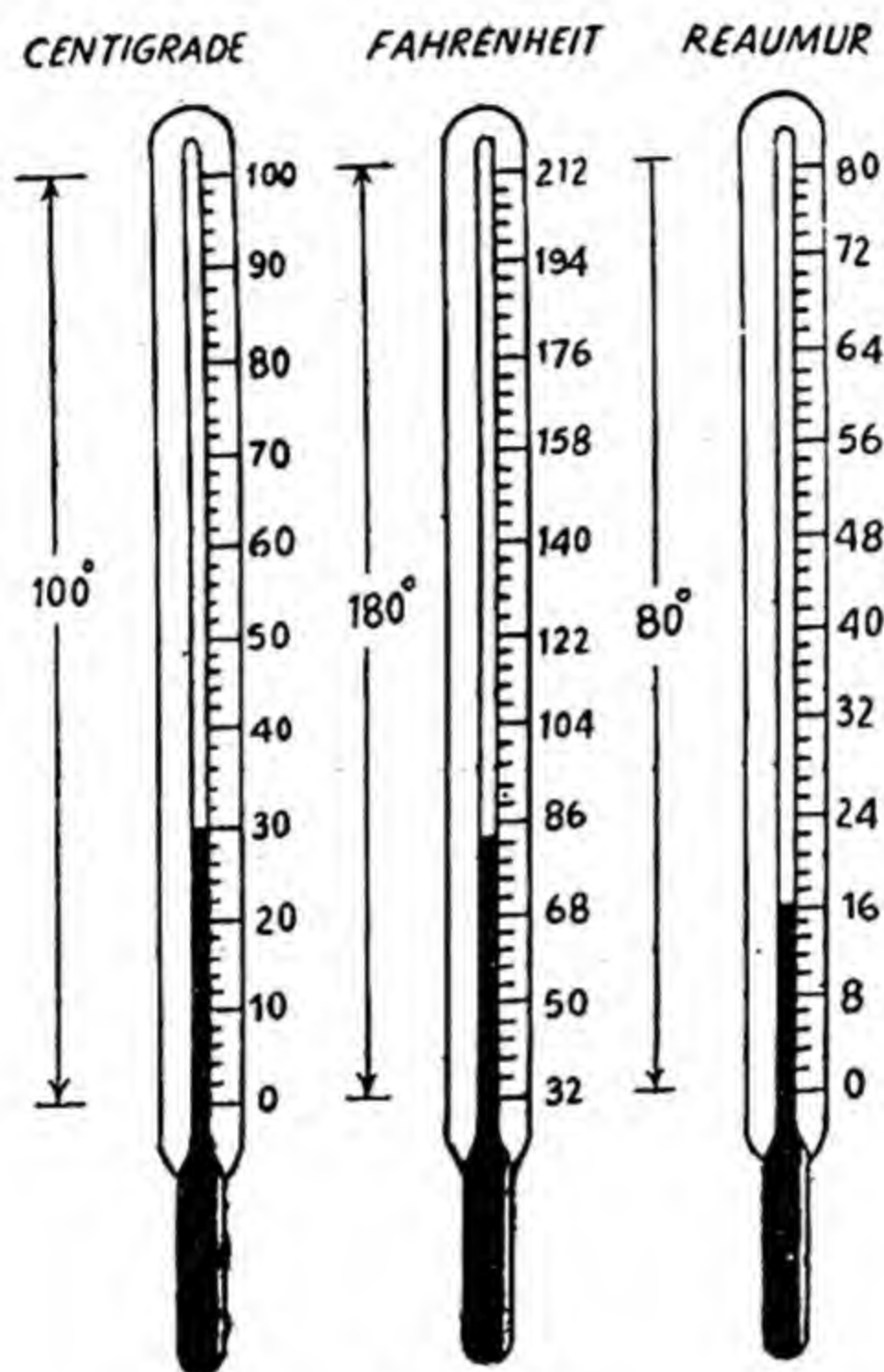


Fig. 12.1.

The numbering may be extended above hundred and below zero.

The range of an ordinary mercury in glass thermometer is limited from -30°C to 250°C , as below -30°C crystals of mercury start forming and above 250°C vapour of mercury collect in the upper space and suppress the level of mercury in the capillary tube. The upper limit can be raised to about 600°C by filling the space above mercury with compressed nitrogen, or CO_2 under high pressure as in this way the boiling point of mercury is raised. The range can be further increased to about 750°C by using tubes of silica.

Mercury thermometers are generally employed for rough work as these suffer from a number of defects. If these are required for the use in very accurate work, then various corrections must be applied to get the true temperature.

The principal sources of error of mercury in glass thermometers are.

- (i) Variation in the bore
- (ii) Effect of external pressure on the volume of the tube
- (iii) Effect of internal pressure
- (iv) Change in the zero reading and in the fundamental interval.
- (v) Exposure of stem of thermometer.
- (vi) Composition of the glass.

Advantages of mercury as a thermometric substance.

1. Mercury boils at 357°C and freezes at -39°C . It remains in the liquid state over a fairly wide range of temperature and thus can be used to measure temperatures as high as 350°C and as low as -32°C .

2. Being a good conductor of heat, it takes up heat quickly from the body whose temperature is to be measured *i.e.* it is quick acting.

3. It has a fairly large coefficient of expansion *i.e.* the increase in volume of a given mass of mercury for every 1°C rise of temperature is fairly large.

4. Its expansion is uniform so that the increase in volume for equal rise of temperature is the same.

5. It has a low thermal capacity, *i.e.*, a very small quantity of heat is required to increase its temperature through a certain range.

6. It has a very low vapour pressure at ordinary temperatures. Thus the space above mercury contains very little quantity of mercury vapour.

7. It is an opaque and a shining liquid and can be easily seen in the glass tube.

8. It can be readily obtained in a pure state.

9. It does not wet the glass tube.

12.4. Alcohol thermometers. Mercury thermometer cannot be used for measurement of very low temperatures as its minimum range is about -32°C . To measure low temperature sometimes alcohol thermometers are used. The alcohol is coloured with some dye so that its level can be easily read in the glass tube. Following are its advantages and disadvantages as a thermometric substance as compared to mercury.

Advantages. (i) Alcohol freezes at -130°C while mercury freezes at -39°C . Alcohol thermometer can thus be used to measure sufficiently low temperatures.

(ii) Expansion of alcohol is much larger than that of mercury for a given rise of temperature. Alcohol thermometer is, therefore,

more sensitive than a mercury thermometer to study temperature variations.

(iii) The thermal capacity of alcohol is greater than that of mercury. For a given volume, alcohol requires much less quantity of heat than mercury to raise its temperature through the same range.

(iv) Alcohol is a light liquid and wets glass. Its motion is, therefore smooth even in a tube of narrow bore, while motion of mercury is jerky.

Disadvantages. (i) Boiling point of alcohol is 78°C . Hence alcohol thermometers cannot be used for the measurement of high temperatures.

(ii) Expansion of alcohol is not uniform. It increases with rise of temperature. An alcohol thermometer, therefore, has to be graduated with respect to a mercury thermometer.

(iii) Alcohol is highly volatile so its vapours readily collect in the space above and exert pressure.

(iv) Alcohol wets the glass surface. When the temperature falls some of the liquid keeps on sticking to the walls.

12.5. Special thermometer. Besides the mercury in glass thermometer some thermometers have been designed to meet requirements of special nature. These have been described in the following articles.

(i) **Clinical thermometer** (*Doctor's thermometer*). This is a form of maximum sensitive thermometer used for recording the temperature of the human body. This type of thermometer is graduated in Fahrenheit scale having a range lying between 95°F to 110°F each degree being divided into five parts. The normal average temperature of a healthy person is taken to be (98.4°F) .

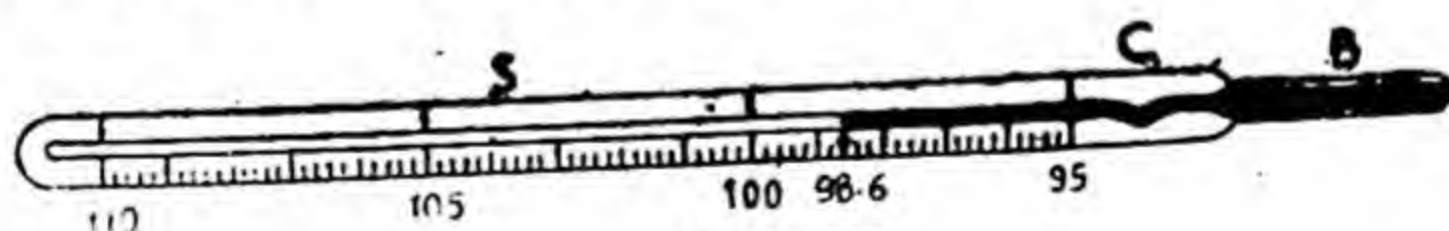


Fig. 12.2

It consists of a thin walled glass bulb *B* connected to a fine, thick walled capillary tube *S* called the stem of the thermometer. There is a constriction *C* in the bore near the bulb.

When the bulb of the thermometer is placed in the armpit or below the tongue, the temperature of the bulb rises and the mercury expands. The force of expanding mercury pushes it through the constriction *C* into the stem and the thread rises to indicate the maximum temperature of the human body.

When the thermometer is removed the temperature falls and the mercury below *C* contracts, the thread breaks at the constriction and leaves the thread above the constriction *C* intact. When the thermometer is to be used again, the thermometer is held from the stem and is given a sharp shake, so that the mercury in the stem passes through the constriction into the bulb.

(ii) **Six's maximum and minimum thermometer.** In this type of thermometer the maximum and minimum thermometers are combined into one piece of apparatus.

It consists of a long cylindrical bulb *A* filled with alcohol connected to another small spherical bulb *E* by a bent U-shaped tube *CD* as shown. The bulb *E* also contains alcohol which does not fill it completely, a space being left for expansion. Part of the U tube *CD* contains mercury which separates the alcohol in the tube between *A* and *C* from the alcohol in the bulb between *E* and *D*. The positions of the mercury threads as at *C* and *D* are indicated by small steel indices provided with light springs to prevent slipping due to their weight. These springs are not so strong that they may oppose the movement of the indices when these are pushed up by the mercury thread. A magnified view of the index is shown separately in the diagram.

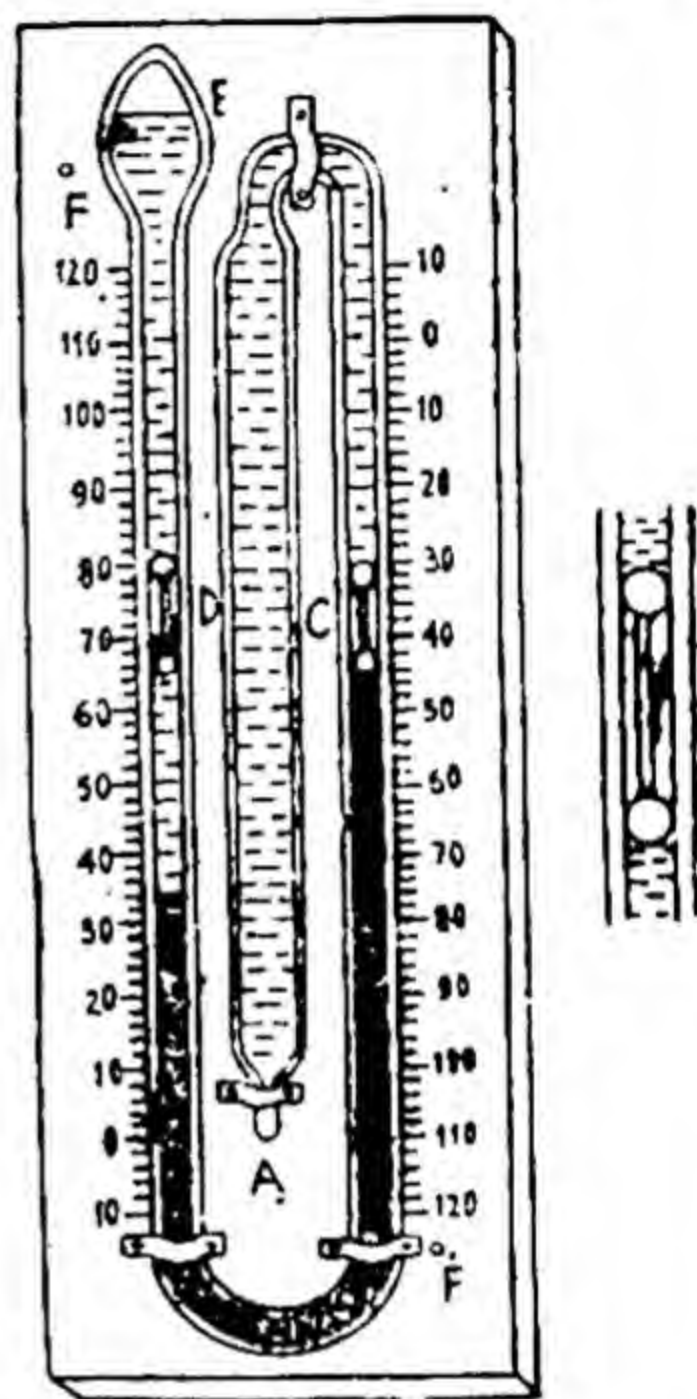


Fig. 12.3

When the temperature rises the alcohol in the bulb *A* expands pushing the mercury thread at *C* downwards and that at *D* upwards. The mercury thread in turn pushes the index at *D* upwards whereas the index at *C* remains in the same position. If the temperature goes on rising the index at *D* goes on moving upward. Hence the scale on this side is marked with zero on the lower side and the highest temperature of 120°F on the upper side.

When the temperature falls the alcohol in *A* contracts. The mercury thread at *C* rises upward and pushes the index. The mercury thread in *D* falls downwards and the index at *D* remains in the same position. If the temperature goes on decreasing the index *C* goes on moving upward. Hence the scale on this side is marked with zero at the top and maximum of 120°F on the lower side.

Thus the maximum temperature during a certain period is indicated by the position of the index on the *D* and the minimum temperature by the position of the index on the side *C*.

The adjustment of the steel indices to bring them in contact with the mercury surface is done with the help of a strong small horse-shoe magnet.

(iii) **Beckmann's Thermometer.** Beckmann's thermometer is a special type of thermometer used for measuring small differences in temperature, correct up to $\frac{1}{10}^{\circ}\text{C}$ or $\frac{1}{100}^{\circ}\text{C}$, in cases where the change in temperature is important, and the knowledge of the actual temperature is not necessary. It consists of a large bulb *A* containing mercury and connected to the capillary stem *B*, graduated with 5 or 6 large divisions each corresponding to 1°C , each division subdivided into 10 or 100 equal parts. To use the thermometer over a large range of temperature, a constricted bulb *C* is provided at the top end of the stem. The bulb *C* forms a chamber into which some of the mercury may be transferred or vice versa, in order that sufficient mercury is left in the bulb *A* to enable the lower temperature to be read, the level being near the foot of the scale at the start. The bulb *A* is immersed in the vessel whose **temperature change** is required, the higher temperature is then read. The difference in the readings gives the required difference in the temperature.

The advantage of this arrangement consists in greater accuracy being obtained without the necessity of employing a very long stem, which gets broken easily.

Other suitable liquids for thermometers are acetone, aniline, glycol, methyl alcohol.

(iv) **Standard constant volume Hydrogen Thermometer.** This thermometer makes use of the changes of pressure of hydrogen while its volume is kept constant.

The standard constant volume Hydrogen thermometer was designed by Harker and Chappius. It consists of a platinum irridium cylindrical bulb *C* of 1 litre capacity. This bulb is about one metre in length and 3.6 cm. in diameter containing *pure dry* hydrogen at a pressure of 100 cms. of mercury at 0°C . The cylindrical bulb is connected by platinum capillary tube one metre long and 0.7 mm in dia. to the manometer which is used to measure the pressure. The manometer consists of two vertical glass tubes *A* and *B* communicating with each other and connected to the reservoir *R* by means of a rubber tube containing mercury. There is a platinum tip P_1 in the tube *A* as shown in Fig. 12.5. The apparatus is also provided with a barometer *D*, the stem of which dips into mercury contained in tube *B*. By bending the stem tube suitably, barometer *D* is placed vertically above the tube *A*. There is a platinum tip P_2 in the tube *D*.

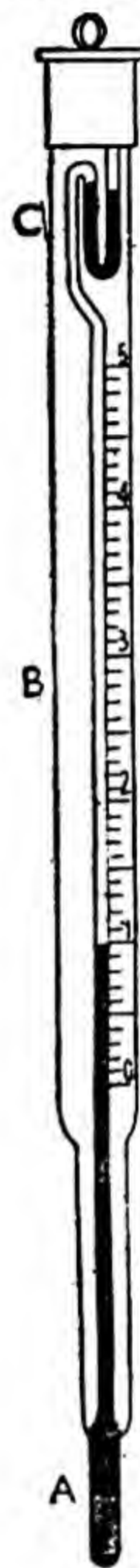


Fig. 12.4.

A scale is placed vertically so that the zero of the scale coincides with

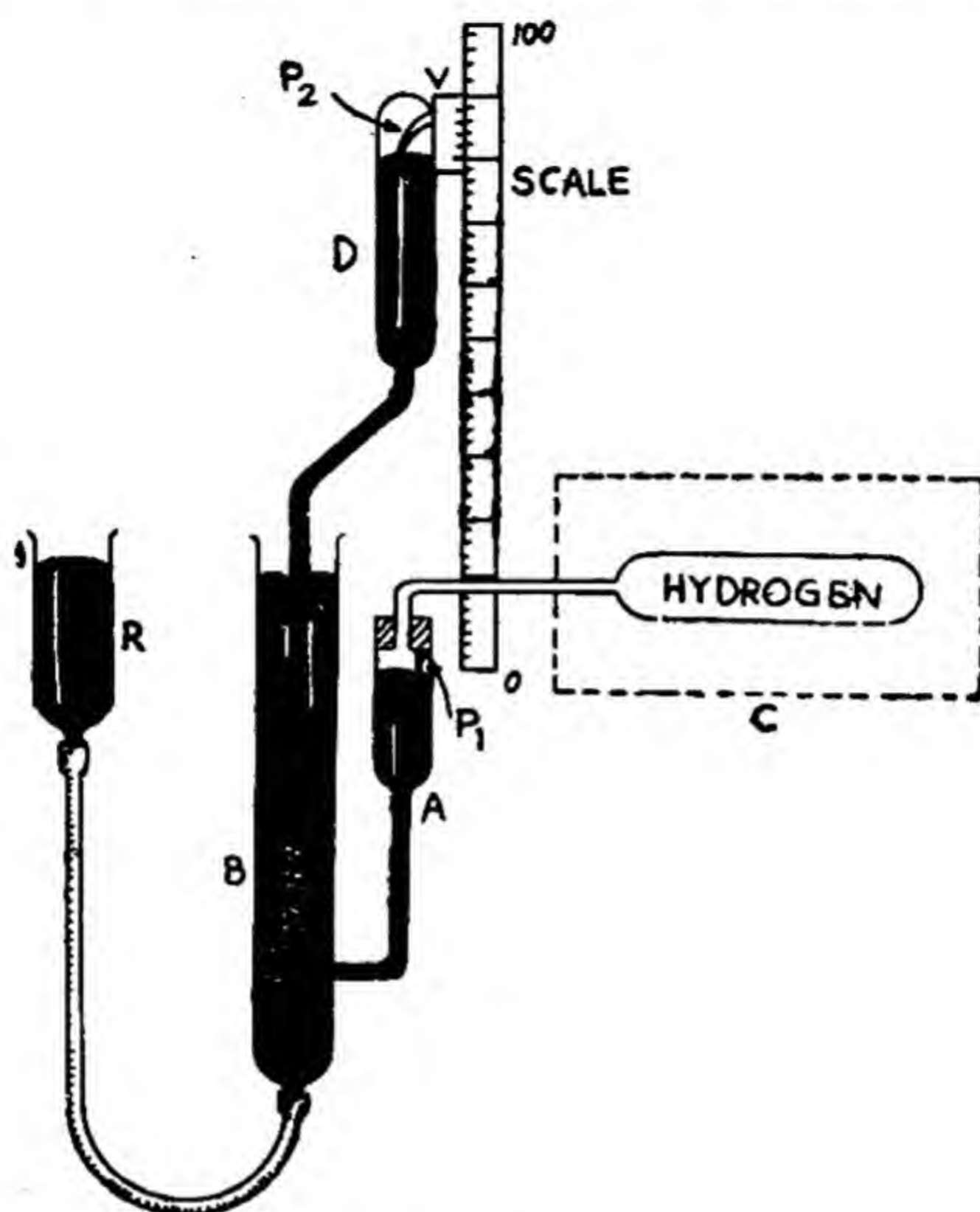


Fig. 12.5.

the platinum tip P_1 . The position of the platinum tip P_2 is read by the vernier V , which can slide along the scale.

Working (i) To perform the experiment surround the cylindrical bulb C with ice. The position of the reservoir R is adjusted so that the mercury in the tube A touches the platinum tip P_1 . Then the barometer D is adjusted by moving it up and down along the scales, so that the mercury in it touches the platinum tip P_2 . The reading of the vernier V is noted along the scale. This gives the pressure P_0 of the gas in the cylindrical bulb C at 0°C . If h_0 is the vertical difference between top of mercury in A and B then $P_0 = P + h_0$, where P is the atmospheric pressure.

(ii) The cylindrical bulb C is now surrounded by steam. The hydrogen gas expands pushing down the mercury in the tube A . The position of the reservoir R and that of the barometer D are again adjusted so that mercury in A touches P_1 and mercury in D touches the tip P_2 . The volume is thus kept constant. The reading of the vernier gives the pressure P_1 of the gas at the temperature of the steam (supposed to be 100°C).

Hence $P_{100} = P + h_{100}$ where h_{100} = vertical difference between A and B .

(iii) The bulb is now surrounded by the bath whose temperature is to be found out and the pressure P_t of the gas in the cylinder C at the unknown temperature is again noted after making the necessary adjustments,

$\therefore P_t = P + h_t$ where h_t = vertical difference between mercury levels between A and B .

Calculations. If γ is the coefficient of increase of pressure at constant volume, then

$$P_{100} = P_o(1 + \gamma 100)$$

$$\text{or} \quad \gamma = \frac{P_{100} - P_o}{P_o \times 100} \quad \dots(i)$$

$$\text{and} \quad P_t = P_o(1 + \gamma t)$$

$$\text{or} \quad \gamma = \frac{P_t - P_o}{P_o \times t} \quad \dots(ii)$$

From (i) and (ii)

$$\frac{P_{100} - P_o}{P \times 100} = \frac{P_t - P_o}{P_o \times t}$$

$$\therefore t = \frac{P_t - P_o}{P_{100} - P_o} \times 100.$$

$$= \frac{(P + h_t) - (P + h_o)}{(P + h_{100}) - (P + h_o)} \times 100 = \frac{h_t - h_o}{h_{100} - h_o} \times 100$$

Corrections. For accurate measurement of temperature, corrections must be applied for the various sources of errors.

(i) The volume of the bulb C is different at different temperatures so that the measurements are not made strictly at constant volume.

(ii) Some gas is absorbed in the walls of the bulb especially at low temperatures.

(iii) The barometer pressure changes as the density of mercury changes with the change in temperature.

(iv) The hydrogen gas is not perfect and deviates slightly from the behaviour of a perfect gas.

Advantages. (1) It has a wide range from -220 to 500°C and with Nitrogen it can be used upto 1600°C .

(2) Since the expansion of hydrogen gas is considerable, the thermometer is very sensitive. It has an accuracy of

(i) 0.005°C between fixed points i.e. between 0°C to 100°C .

(ii) 0.1°C upto 500°C .

(iii) 2°C upto 1600°C .

(3) Unlike mercury thermometer, readings on different gas thermometers using the same gas agree among themselves. This is because,

(i) gas can be obtained in pure form.

(ii) expansion of the cylindrical bulb does not materially affect the readings.

(4) Its readings agree with thermodynamic scale (of Lord Kelvin) which is the ultimate standard of reference. That is why this thermometer is quite suitable as a standard of reference.

Disadvantages.

(i) The thermometer is slow in action.

(ii) It cannot be used for the direct measurement of temperature as its bulb is too large.

(iii) It cannot be used for measuring varying temperatures.

Example 1. The pressures of the gas in a constant volume gas thermometer are 100 cms. and 136.99 cms. of mercury at 0°C and 100°C respectively. When the bulb is placed in a bath the pressure is 125.8 cms. of mercury. Calculate the temperature of the bath.

Here

$$P_0 = 100 \text{ cms.}$$

$$P_{100} = 136.99 \text{ cms.}$$

$$P_t = 125.8 \text{ cms.}$$

If $t^{\circ}\text{C}$ is the temperature of the bath, then

$$\begin{aligned} t &= \frac{P_t - P_0}{P_{100} - P_0} \times 100 \\ &= \frac{125.8 - 100}{136.99 - 100} \times 100 \\ &= \frac{25.8}{36.99} \times 100 = 69.74^{\circ}\text{C}. \end{aligned}$$

12.6 Pyrometers. Pyrometry is the name given to that branch of science which deals with the measurement of high temperature, and the instruments used are called **pyrometers**. They were principally designed and developed for temperatures beyond those that can be measured by the usual mercury thermometers, but they can also be used, to measure moderate as well as low temperatures.

There are three types of pyrometers in general use :—

(i) Resistance pyrometers for temperatures ranging from -200°C to 1300°C . The example is *Platinum resistance thermometer*.

(ii) Thermo electric pyrometers for temperatures up to 3000°C . The example is *thermo electric thermometer*.

(iii) Pyrometers which measure high temperatures upto the order of 3200°C by the method of radiation. There are two types in practice :

(a) Total radiation pyrometers, range is up to 1500°C .

(b) Optical Pyrometers, range is up to 3200°C .

(i) **Platinum-resistance Thermometer.** The first resistance thermometer was constructed by Sir William Siemens in 1871. The platinum thermometer is due to Callender and Griffiths and it gives quite reliable results over a wide range of temperatures. Platinum has been chosen as thermoelectric substance because of,

- (i) its high melting point
- (ii) Chemical stability at high temperatures
- (iii) its availability in pure state, and
- (iv) its large temperature range.

Principle. The variation of electrical resistance with temperature has been made use of for the measurement of temperature in a platinum resistance thermometer. The resistance of pure platinum is found to vary according to the formula

$$R_t = R_0 (1 + \alpha t + \beta t^2)$$

where α and β are constants and R_t and R_0 are the resistances at $t^{\circ}\text{C}$ and 0°C respectively.

For pure platinum $\alpha = 3.94 \times 10^{-3}$ and

$$\beta = -5.8 \times 10^{-7}.$$

The values of α and β are determined by finding the resistance of the platinum coil at.

- (a) Melting point of ice i.e., at 0°C
- (b) Boiling point of water i.e., at 100°C and
- (c) Boiling point of sulphur i.e. at 444.6°C .

Clausius showed that for a conductor

$$R_t = R_0 (1 + \alpha t)$$

where R_t is the resistance of the conductor at $t^{\circ}\text{C}$

R_0 is the resistance of the conductor at 0°C

α is the coefficient of increase of resistance. For platinum free from all impurities, the Clausius simple formula given above holds good. Now if the resistance R_0 , R_{100} and R_t of a piece of platinum are found at 0°C , 100°C and $t^{\circ}\text{C}$, respectively, then

$$R_t = R_0 (1 + \alpha t)$$

or $R_t - R_0 = R_0 \alpha t$

$$R_{100} = R_0 (1 + \alpha 100)$$

...(i)

$$\text{or } R_{100} - R_0 = R_0 \alpha \cdot 100 \quad \dots (ii)$$

Dividing (i) by (ii) we have

$$\frac{R_t - R_{100}}{R_{100} - R_0} = \frac{t}{100}$$

$$\text{or } t = \frac{R_t - R_0}{R_{100} - R_0} \times 100$$

This value of t is correct on what is called *Platinum* scale and this temperature is termed as *Platinum temperature* denoted by t_p .

$$\therefore t_p = \frac{R_t - R_0}{R_{100} - R_0} \times 100 \quad \dots (iii)$$

The quantity $R_{100} - R_0$ is known as the fundamental interval of the thermometer.

The temperature on the *platinum* scale differs from the temperature on the perfect gas scale or absolute scale.

To get the true temperature t from the observed temperature t_p , Callender has deduced the following relation

$$t - t_p = \delta \left[\left(\frac{t}{100} \right)^2 - \frac{t}{100} \right] \quad \dots (iv)$$

Where δ is a constant for the particular specimen of platinum wire used. Its value is very nearly 1.5. To prove relation (iv), we have

$$t - t_p = t - \frac{R_t - R_0}{R_{100} - R_0} \times 100 \quad \therefore t_p = \frac{R_t - R_0}{R_{100} - R_0} \times 100$$

$$= t - \frac{R_0 (\alpha t + \beta t^2)}{R_0 (100 \alpha + (100)^2 \beta)} \times 100$$

$$\therefore R_t = R_0 (1 + \alpha t + \beta t^2)$$

$$\text{or } R_t - R_0 = R_0 (\alpha t + \beta t^2)$$

$$\text{and } R_{100} - R_0 = R_0 (\alpha \cdot 100 + \beta (100)^2)$$

$$\therefore t - t_p = t - \frac{t (\alpha + \beta t)}{(\alpha + 100 \beta)}$$

$$= \frac{1}{\alpha + 100 \beta} [t (\alpha + 100 \beta) - t (\alpha + \beta t)]$$

$$= \frac{\beta}{\alpha + 100 \beta} (100 t - t^2)$$

$$= - \frac{\beta (100)^2}{\alpha + 100 \beta} \left[\left(\frac{t}{100} \right)^2 - \left(\frac{t}{100} \right) \right]$$

$$\therefore t - t_p = \delta \left[\left(\frac{t}{100} \right)^2 - \left(\frac{t}{100} \right) \right]$$

$$\text{where } \delta = - \frac{\beta (100)^2}{\alpha + 100 \beta}$$

As β is negative quantity δ is positive.

Construction. It consists of a platinum wire free from impurities like silicon, carbon, copper, tin etc, doubled on itself to avoid induction effects, wound on a thin plate of mica, enclosed in a porcelain tube as shown in Fig. 12.6. The ends of the platinum wire are attached to platinum leads which pass through holes in mica discs closely fitting in the upper part of the tube. The free ends T_1 and T_2 of the leads are connected to the terminals at the top of the instrument for connections to the external circuit. The mica discs are used for insulating the wires passing through them and for preventing convection currents from moving up and down the tube.

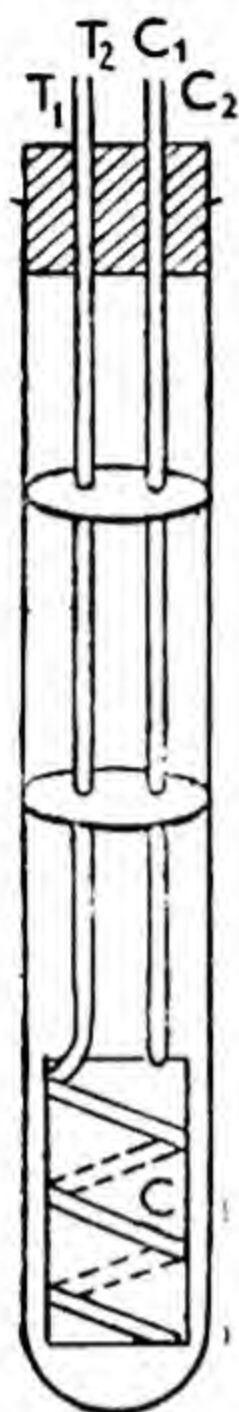


Fig. 12.6

As the lead wires are long enough, they offer appreciable resistance which will increase with temperature and so introduce errors. To compensate for the resistance of leads, an exactly similar pair of leads C_1, C_2 with their lower ends joined together are placed close to the platinum thermometer leads as shown. The tube is sealed at the top to protect the platinum coil from the effect of moisture etc.

Working. The resistance of the wound platinum coil is found with the help of a modified form of Wheatston's Bridge as shown in Fig. 12.7. The ratio arms P and Q are of equal resistances. The leads T_1, T_2 are connected in the arm X and compensating leads C_1, C_2 are connected

in the arm R . The resistance of platinum changes roughly by 0.01 ohm per degree centigrade. In a resistance box, steps of such a low resistance are not possible, hence a wire of uniform area of cross-section, of length $2a$ and resistance ρ ohms per centimeter is inserted as shown. Such an arrangement is known as *Callendar and Griffith's Bridge*.

When platinum wire is at 0°C , value of R is so adjusted that the balance point is obtained at the mid-point of wire $2a$. If the values of resistances in arms P and Q are kept equal, then

Resistance in X arm = resistance in R arm.

$\therefore X + \text{resistance of leads} + R_0 + a\rho = R + a\rho + \text{resistance of compensating leads}$

or

$$R_0 = R - X$$

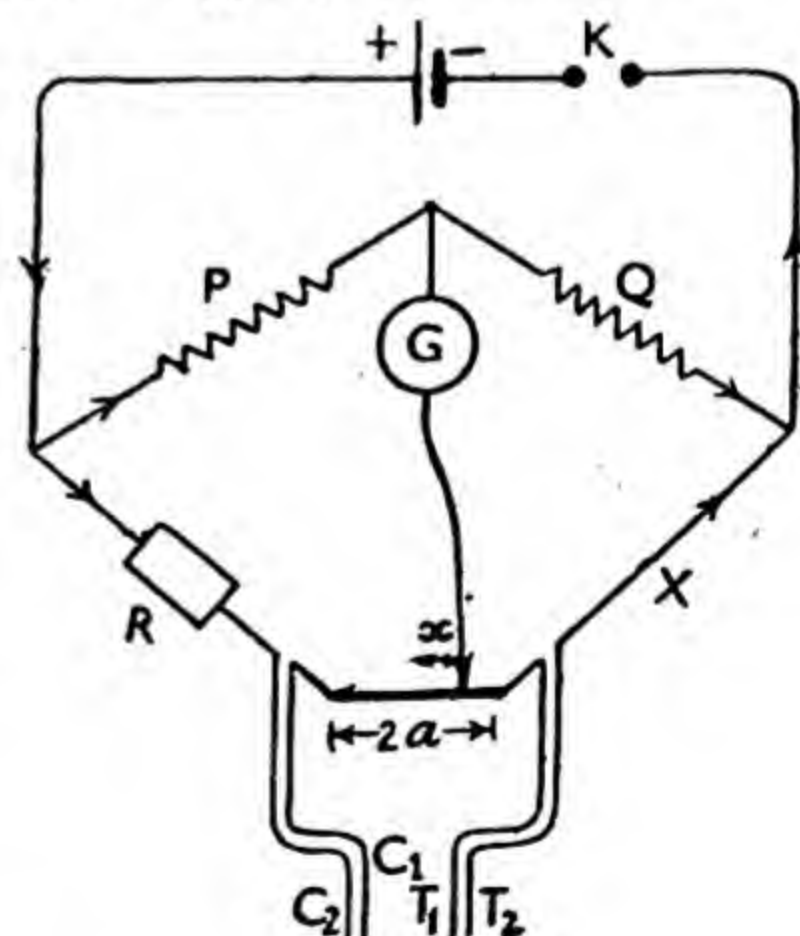


Fig 12.7

When the platinum coil is placed in a bath at $t^{\circ}\text{C}$, its resistance increases from R_0 to R_t . The balance point will then shift towards the side of the platinum thermometer thereby decreasing the resistance on the side of X and increasing the resistance on the side of R by an equal amount. If a new balance point is obtained at a distance x from the middle point which is marked zero, then

$$R_t + (a - x)\rho = R + (a + x)\rho.$$

$$\therefore R_t = R + 2x\rho.$$

Knowing x and ρ , R_t can be calculated. Similarly the resistance of platinum thermometer at 100°C i.e., R_{100} is found by placing the thermometer in a steam bath.

Knowing R_0 , R_t and R_{100} the temperature on the platinum scale is found by using relation (iii) and then true temperature is determined by using relation (iv) if the value of δ is known.

Range of platinum Thermometer. This thermometer can be reliably used from -200°C to 1300°C . Its readings are accurate to 0.01°C upto 500°C and to 0.1°C upto 1300°C .

Advantages.

1. It has a wide range i.e., from -200°C to 1300°C .
2. It is correct to 0.01°C up to 500°C and to 0.1°C up to 1300°C .
3. It is very convenient to use and when once standardised by comparison with a gas thermometer, it serves as a reliable secondary standard of reference.
4. It is free from zero error, because the resistance of the pure and well annealed platinum wire is always the same at the same temperature.
5. "Stem Correction" has been eliminated in it by the use of compensating leads.
6. The temperature can be measured sitting quite far off from the furnace etc, by just increasing the length of the leads.

Disadvantages.

1. It has large thermal capacity.
2. Porcelain being not a good conductor, takes a long time to attain the temperature of the bath and is therefore unfit to measure rapidly changing temperatures.
3. It is not suitable for measuring unsteady and rapidly varying temperatures.
4. The size of the tube is large and hence is not suitable for measuring at a point on a hot source.
5. The tube is fragile and cannot withstand mechanical shocks.

Example 2. The values of R_0 , R_{100} in a platinum resistance thermometer are 2.585 , 3.510 ohms respectively. When it was placed in a furnace,

the resistance R was found to be 9.098 ohms. Calculate correct up to 1°C the temperature of the furnace on the hydrogen scale. Given that δ for specimen of platinum is 1.5 .

The temperature on the platinum resistance scale is given by

$$t_p = \frac{R_t - R_o}{R_{100} - R_o} \times 100$$

Now

$$R_o = 2.585 \Omega$$

$$R_{100} = 3.510 \Omega$$

$$R_t = 9.098 \Omega$$

$$\therefore t_p = \frac{9.098 - 2.585}{3.510 - 2.585} \times 100 = 704^\circ\text{C}.$$

$$\text{Again } t - t_p = \delta \left[\left(\frac{t}{100} \right)^2 - \left(\frac{t_p}{100} \right)^2 \right]$$

$$t - 704 = 1.5 \left[\left(\frac{t}{100} \right)^2 - \left(\frac{704}{100} \right)^2 \right]$$

$$\text{or } t - 704 = 0.00015 t^2 - 0.015 t$$

$$\text{or } 0.00015 t^2 - 1.015 t + 704 = 0$$

This is a quadratic equation which can be solved in a usual way.

$$\begin{aligned} \therefore t &= \frac{1.015 \pm \sqrt{(1.015)^2 - 4 \times 0.00015 \times 704}}{2 \times 0.00015} \\ &= \frac{1.015 \pm \sqrt{0.61}}{0.0003} = \frac{1.015 \pm 0.78}{0.0003} \\ &= 5984^\circ\text{C} \text{ or } 784^\circ\text{C}. \end{aligned}$$

Example. 3. A fixed mass of a gas maintained at a constant pressure occupies 200.0 c.c. at the temperature of melting ice, 273.2 c.c. at the temperature of water boiling under normal pressure, and 525.1 c.c. at the normal boiling point of sulphur. A platinum wire has resistance of 2.000 , 2.778 and 5.280 ohms respectively at the same temperature. Calculate the value of boiling point of sulphur given by the two sets of data.

(i) On Constant pressure thermometer

$V_o = 200$ c.c. $V_{100} = 273.2$ c.c., $V_t = 525.1$ c.c. where t is the boiling point of sulphur on the gass scale.

$$\therefore t = \frac{V_t - V_o}{V_{100} - V_o} \times 100 = \frac{525.1 - 200}{273.2 - 100} \times 100 = 444.2^\circ\text{C}.$$

(ii) On platinum resistance thermometer.

$$R_o = 2.00 \Omega, R_{100} = 2.778 \Omega \text{ and } R_t = 5.28 \Omega.$$

THERMOMETRY

$\therefore t =$ The boiling point of sulphur on the platinum scale

$$= \frac{R_t - R_0}{R_{100} - R_0} \times 100 = \frac{5.280 - 2.000}{2.778 - 2.000} \times 100 = 421.6^\circ\text{C}.$$

12.7. Seebeck effect. This phenomenon was discovered by Seebeck in 1821. If two dissimilar metals (Cu and Fe) are joined to form two junctions as shown in Fig. 12.8 and one of the junctions is kept cold while the other is heated, an electric current starts flowing through the metals as indicated by a galvanometer and hence an e.m.f. is developed across the two junctions.

Seebeck

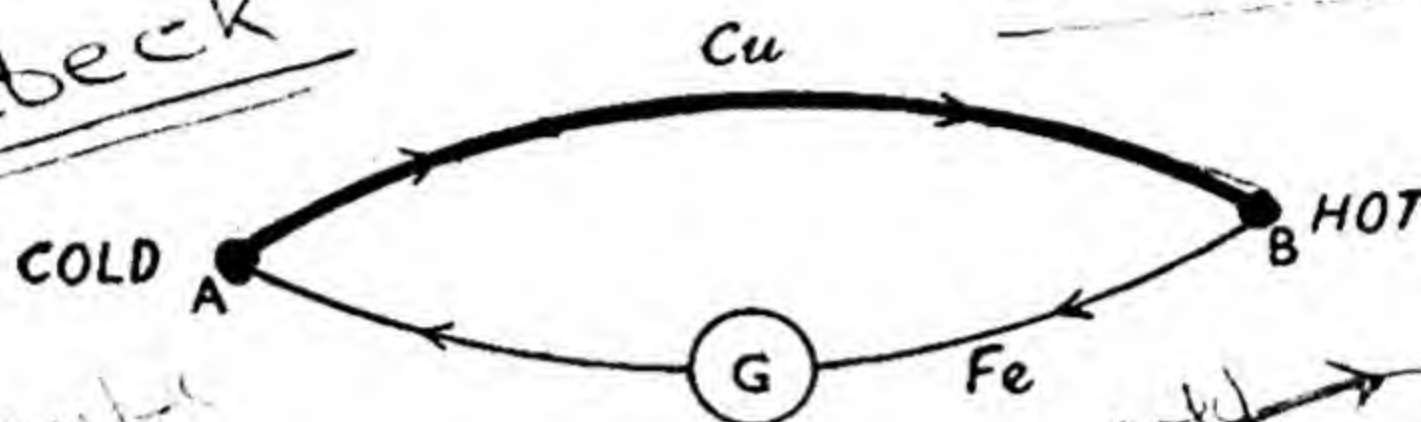


Fig. 12.8.

The current flows from (Cu) to Fe at the hot junction B. This current is called thermo-electric current and the corresponding E.M.F. is known as Thermo-e.m.f. The arrangement is known as **thermo-couple**. The production of thermo e.m.f. by a thermo couple when one of the junctions is heated keeping the other cold is known as **Seebeck effect**. The thermo e.m.f. generated depends upon

- (i) Nature of the two metals forming thermo couple
- (ii) Temperature difference between hot and cold junctions.

Seebeck effect

It is preferable to measure e.m.f., instead of circuit current: because the e.m.f. developed depends on the temperature difference: only where as the current depends upon the resistance of the circuit which alters considerably with temperature.

Effect of temperature. If the graph is plotted between thermo e.m.f. E and temperature t , it is of the parabola type as shown in Fig. 12.9 and it obeys the relation.

$$E = at + bt^2$$

where a and b are constants of the metals forming the thermo couple.

If the end A is kept cold and the temperature of the junction B is slowly increased the thermo-electric current continuously increases. For small difference of temperature, the thermo e.m.f. is proportional to temperature. For large difference of temperature e.m.f. first increases and for a certain temperature of the hot junction it becomes.

a maximum. This temperature is known as *neutral temperature* and is defined as that temperature of the hot junction at which maximum current flows. It is constant for a given couple and depends upon the pair of metals chosen but is independent of the temperature of the cold junction. For example, the neutral temperature for Cu-Fe thermo couple is 270°C whatever the temperature of the cold junction may be.

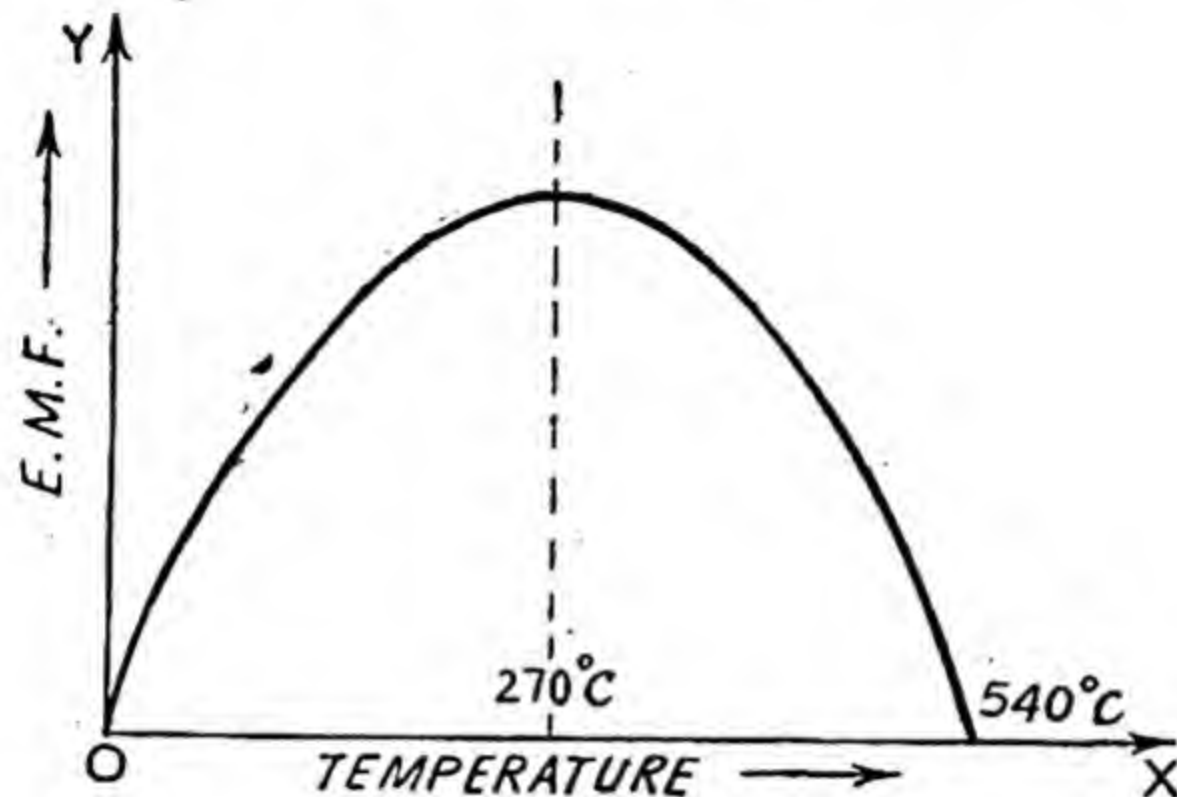


Fig. 12.9.

If the temperature of the hot junction is further increased the thermo electric current (or thermo *e.m.f.*) decreases and finally becomes zero at a temperature known as the *temperature of inversion*. The temperature of inversion is as much above the neutral temperature as the latter is above that of the cold junction. For example when the temperature of the cold junction is 0°C the temperature of inversion is 540°C but if the temperature of the cold junction is 40°C the temperature of inversion is 500°C for Cu-Fe thermo couple. If the temperature is further increased the thermo electric current increases in the opposite direction as shown.

The thermo couple if worked on the rising portion of the curve, where the thermo *e.m.f.* is almost linear function of the temperature, it can be easily adopted as a thermometer to measure any unknown temperature.

(i) **Thermo-electric Thermometer.** Although it is inferior to platinum resistance thermometer for temperature below 100°C but is much more sensitive and reliable for higher temperatures. The maximum temperature up to which it can reliably measure is 3000°C which is much higher than platinum thermometer.

Principle. It makes use of *Seebeck effect* or *thermo electricity* which has been explained in the preceeding Art 12.7 To adopt a thermo couple as a thermometer following points have to be taken into consideration.

1. Selection of suitable metals. Choice of metals for the thermo couples chiefly depends on the temperature to be measured. The metals chosen should be such that the range of temperature for which they are to be used should be quite lower than the neutral temperature. Some of the couples in common use are

(a) Base-metal Couples.

(i) *Copper-constantan* and *iron-constantan* couples do quite well from 200°C to 400°C , both in the laboratory and for industrial work because they develop large *e.m.f.* of the order of 40 to $60\ \mu\text{V}/^{\circ}\text{C}$ and their temperature versus *e.m.f.* curves are practically linear.

(ii) *Iron-nickel* couples can be used up to 800°C . Their temperature versus *e.m.f.* relationship is also nearly linear over this range.

(iii) *Nickel chromium, Nickel-aluminium couple.* Nickel chromium consists of 90% of Ni and 10% Cr; Nickel aluminium consists of about 95% Ni and 5% Al with Si and Mn. This combination has the commercial name of chromel—Alomel thermo couples and can be used up to 1200°C .

[Note. Small quantities of Si and Mn are necessary to reduce the brittleness at lower temperatures.]

The advantages of using these metals is that they give a relatively large *e.m.f.* per degree and their cost is low so that heavy sections can be employed, giving low resistance.

For high temperatures however, 1200°C to 3000°C these base metals are not satisfactory as they are easily oxidised and Noble-Metal couples are used.

(b) Noble-Metal Couples.

(iv) Platinum-iridium or Platinum-Rhodium couples may be used upto 1750°C .

(v) Thermo-couples of iridium and an alloy of iridium and rutherfordium (90% Ir and 10% Ru) can be used upto 2100°C .

(vi) Tungsten—Molybdenum couples are the best for higher temperatures upto 3000°C .

These couples must be carefully protected from reducing gases and metallic vapours. They are rather costly and the *e.m.f.* developed per degree is about fifth of that couples made of base metals.

Construction. In a thermoelectric thermometer two wires of suitable materials depending upon the temperature to be measured are

welded together at one end. The welded end forms the hot junction. The two wires are insulated from one another by passing them through thin tubes of clay or hard glass and are threaded through mica discs to keep them in position. This is further enclosed in an outer protecting tube of porcelain, quartz or hard glass depending upon the temperature to be measured and provided with a box wood head fitted with terminals T_1 and T_2 to which the wires forming the thermo couple are connected.

To these terminals are connected flexible compensating leads of the same materials as the elements of the couple itself. In this way the cold junction is transferred to a convenient distant place where a constant temperature generally 0°C is maintained as shown in Fig. 12.10.

Working (i) For obtaining higher accuracy the thermo *e.m.f.* is measured with the help of a potentiometer and a standard cell. The connections are made as shown in Fig. 12.11 where AB is a **potentiometer wire** of resistance 1 ohm per metre. With the plug placed in between the studs b and c of the two way key, the standard cell is first put in the circuit and the balance point for it is obtained, say at D , on the potentiometer wire by adjusting the values of the resistance R_1 and R_2 so that, total resistance $R_1 +$ that of the portion AD of the potentiometer wire

$$= 1018.3 \text{ ohms.}$$

Then, since the *e. m. f.* of the standard cell is 1.0183 volts, it is clear that the current flowing through the potentiometer wire is

$$\frac{1.0183}{1018.3} = 1 \text{ milli ampere.}$$

Therefore, obviously fall of potential across one length of the wire

$$\begin{aligned} &= 1 \text{ mill-ampere} \times 1 \text{ ohm} = 10^{-3} \times 1 \text{ Volt} \\ &= 1 \text{ milli-Volt.} \end{aligned}$$

And, therefore fall of potential across 1 mm. length of the potentiometer wire

$$= \frac{10^{-3}}{1000} = 10^{-6} \text{ volt} = 1 \text{ micro-Volt.}$$

It is clear that potential differences of the order of 1 micro-volt can be measured in this manner.

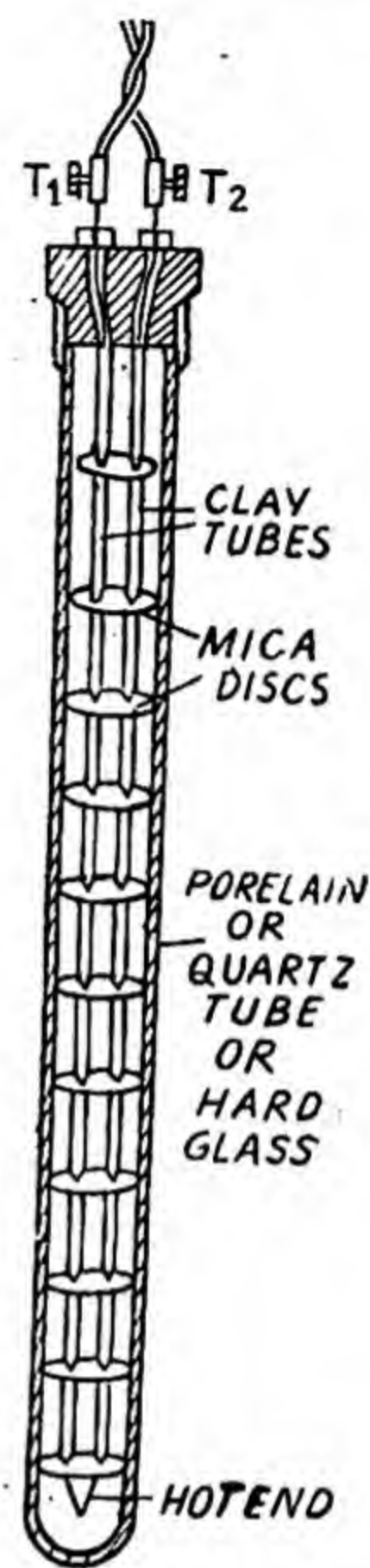


Fig. 12.10

The standard cell is now thrown out of the circuit and the thermo-couple, with its hot junction in the bath or in contact with

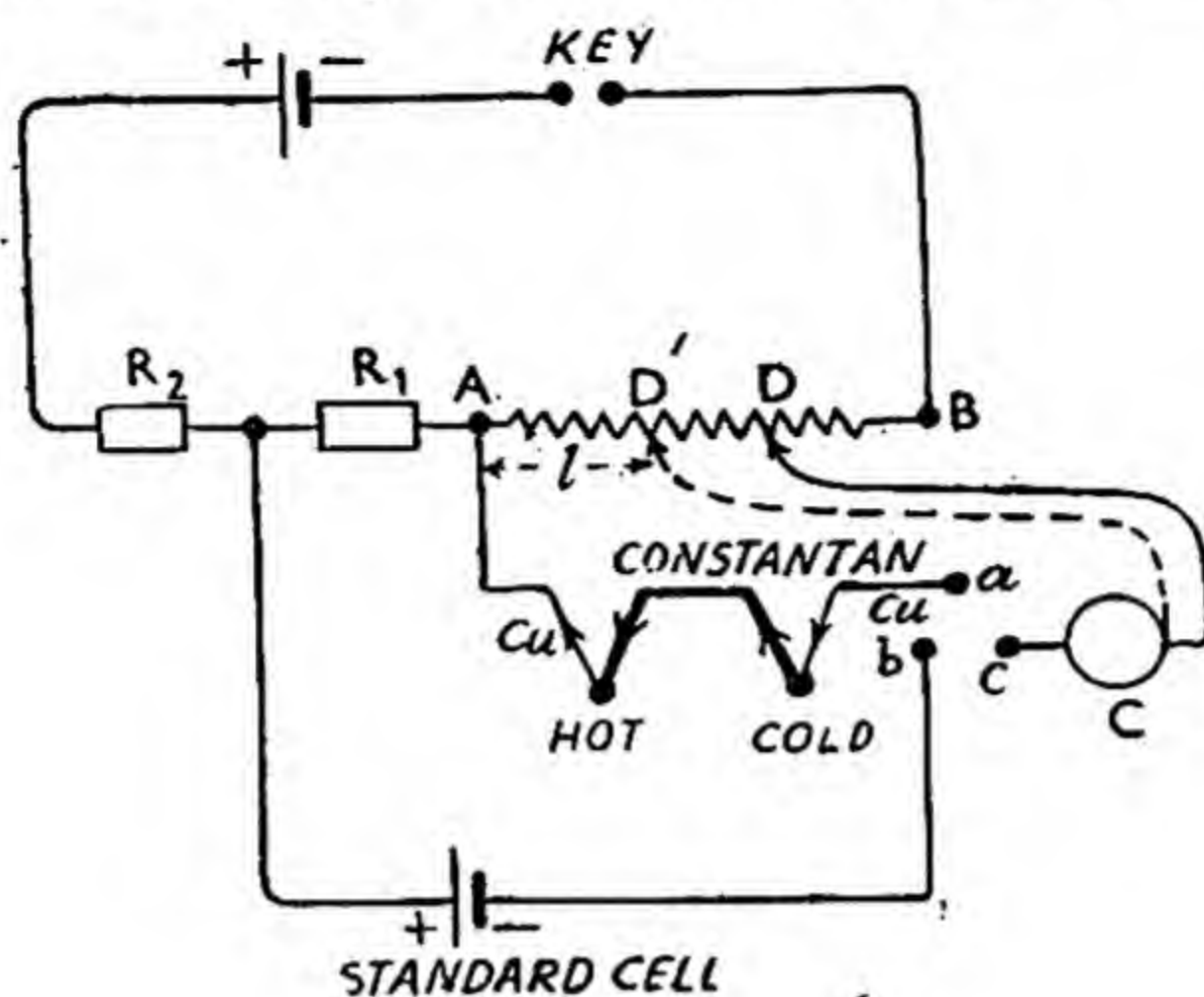


Fig. 12.11.

the given body and its cold junction at 0°C , is taken into circuit by putting in the plug between a and c instead of between b and c , and the balance point on the potentiometer wire obtained as before. Let it be at D' , at a distance l mm from the zero point A .

\therefore $E.M.F$ of the thermo couple $= l \times 10^{-6}$ Volt.

Thus with a potentiometer the $E.M.F.$ can be measured correct up to a micro volt which corresponds to about 10°C for Platinum, Platinum

Rhodium thermo couple and $\frac{1}{40}^\circ\text{C}$

for a Copper constantan thermo couple. To deduce the temperature from the experimental value of $e.m.f.$ a calibration curve is generally supplied by the manufacturers. The calibration curve is drawn between thermo $e.m.f.$ and temperature of the hot junction. The calibration curve of the thermo couple is drawn as follows. The hot junction of the thermometer is put in a bath whose temperature can be varied. The $e.m.f.$ so developed by the thermo couple is measured as discussed above. The calibration curve as shown in Fig. 12.12 is then drawn. After this has been done for a particular thermo couple, then an known temperature can be read off corresponding to the $e.m.f.$ at that temperature.

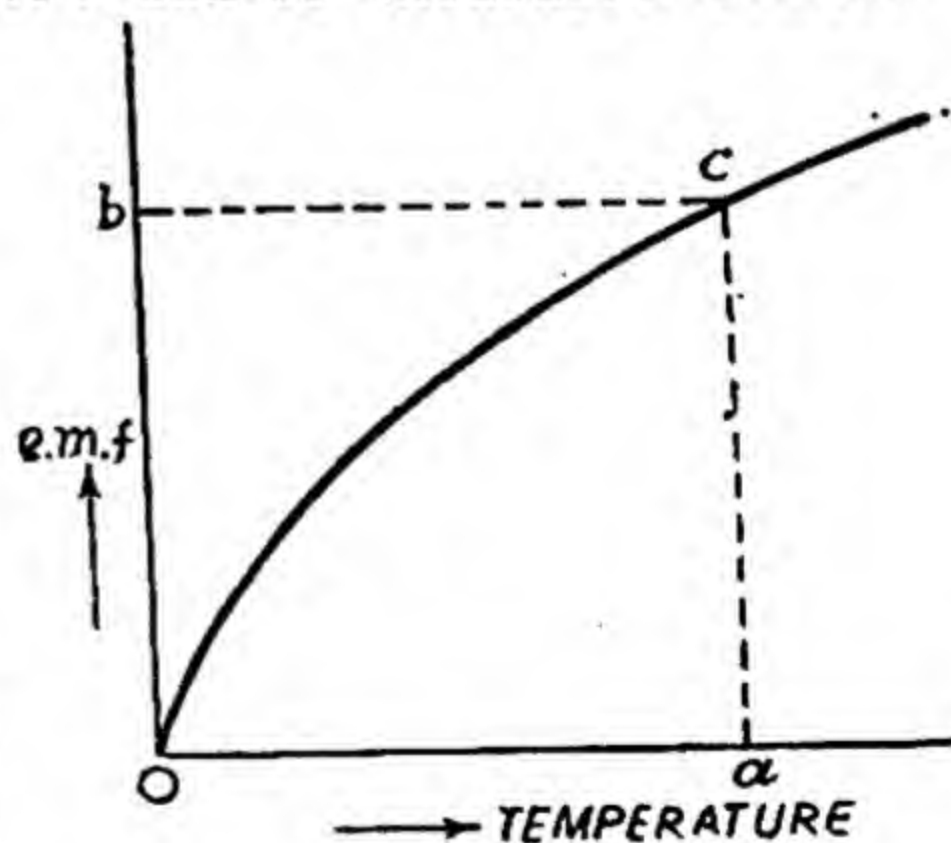


Fig. 12.12.

(ii) To determine the temperature of the hot junction the *e.m.f.* developed by the thermo couple is measured by milli voltmeter graduated to read the temperatures directly. The milli voltmeter used should be of high resistance so that the increase of resistance of the leads or thermo couples does not effect the total circuit resistance appreciably. Though a direct reading and convenient arrangement, its accuracy is limited to within $\pm 5^{\circ}\text{C}$. It is therefore, suitable only for industrial concerns where no great accuracy is required. For higher accuracy, it is necessary to use a suitable potentiometer as discussed above in details.

Advantages. (i) They are quite cheap and can be easily constructed. Hence they are frequently used for laboratory work.

(ii) Their thermal capacity being small, there is no time lag and they are very well suited for measuring rapidly varying temperatures.

(iii) They can be used for measuring temperature at a point.

(iv) They can measure temperatures over a wide range from -200°C to 1600°C and even extending upto 3000°C with suitable thermo-elements.

(v) They are best suited for remote indication and recording. Thus one junction of the thermo couple may be at the top of the mountain and the other at a convenient place in the valley below.

(vi) They can be made direct reading.

Disadvantages. (i) Each thermometer requires a separate calibration as there is no theoretical relation which exists over a wide range.

(ii) The difficulty of maintaining the cold junction at a fixed temperature throughout and the difficulty of applying necessary correction if it be not at 0°C .

(iii) Parasitic electro-motive forces developed in the circuit due to Peltier and other effects.

(iv) Leakage from the mains or furnace circuit. The presence of leakage current can be detected by short-circuiting the thermo couple when the galvanometer continues to be deflected.

(v) They are not so accurate at low temperatures.

Applications. (i) They are widely used in industry for measuring temperatures of gas, blast and other furnaces.

(ii) They can also record temperatures of heated surface under working conditions in paper, textile and rubber industries.

(ii) **Total radiation Pyrometers.** In these instruments the total energy of radiations emitted by a source is measured and the temperature deduced by the application of **Stefan's Law**. Fery's total radiation pyrometer is an example.

(i) **Fery's total radiation pyrometer.** A standard form of total radiation pyrometer designed by Fery is shown in the Fig. 12.13. It

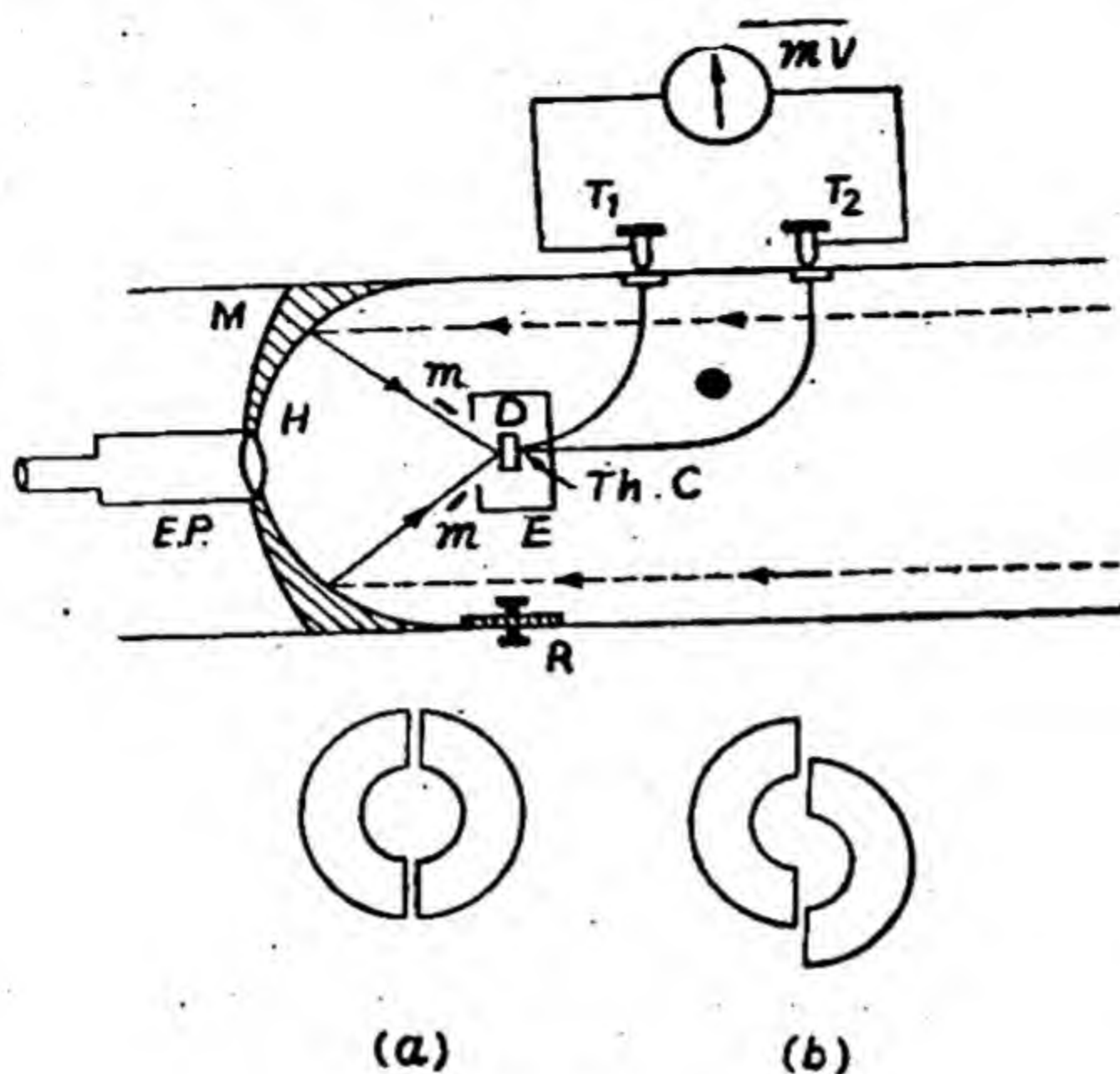


Fig. 12.13

consists of a concave mirror M made of copper with front side nickled and having a small opening H in the centre. In front of the mirror is placed a small diaphragm D backed by a blackened receiving surface. One junction of a thermo-couple is attached to the back surface and the other junction is shielded from the direct radiations by means of tongue and a box. The leads from the thermo-couple are joined to a millivoltmeter mV and the electro-motive force developed is thus determined.

The mirror M can be moved by a rack and pinion arrangement so as to focus the image of the opening in the furnace on the diaphragm. To find if the focussing is correct, the two halves of the diaphragm are polished in front to form a mirror. These halves are inclined to each other at an angle of 5° to 10° . The diaphragm is viewed with the help of an eyepiece $E.P.$ through the opening in the concave mirror. When focussing is perfect the images of the two halves overlap exactly to form a complete circle but when the focussing is imperfect the two halves appear to be displaced as shown.

If the heat image formed by the concave mirror is larger than the hole in the diaphragm D , then the reading of the pyrometer is independent of its distance from the furnace. This result can easily be deduced theoretically. When the distance between the mirror and the furnace be doubled, the total amount of heat radiations

received by the concave mirror is reduced to $\frac{1}{4}$ according to the inverse square law. But at the same time the area which the image covers is also reduced to one-fourth. Hence the amount of radiation received and the area over which it is concentrated decreases in the same ratio. Thus we see that the amount of radiations received per unit area per second is constant and so the reading of the millivoltmeter remains unchanged.

It is a simple matter to find the relation between the size of the object (furnace aperture) and the distance for this type of pyrometer. When the furnace is at a given distance the size of the furnace aperture, necessary to fill the opening in diaphragm completely, can be calculated from the geometry of the Fery's optical system and hence is adjusted accordingly. After this adjustment, the readings of the instrument become independent of its distance from the object.

Calculation of Temperature.

Let T_0 be the temperature of the hot junction S .

T be the unknown temperature of the hot body.

V be the reading of the milli-voltmeter.

Then by applying Stefan's Law, reading of the voltmeter is given by

$$V = \alpha(T^b - T_0^b)$$

where b is a constant and varies from 3.8 to 4.2. Because of this variation from Stefan's fourth power law, the instrument has to be calibrated by sighting it on a standard hot body which is raised to various temperatures. The temperatures are measured by a standard thermo-couple and the corresponding readings of the millivoltmeter are noted. The calibration curve is thus drawn and the unknown temperature can then be read from this calibration curve.

Advantages. (a) The instrument is direct reading and quick acting.

(a) It is robust and has arrangement to render the readings independent of the distance between the instrument (pyrometer) and the object (hot body) within certain limits.

(ii) **Disappearing Filament optical Pyrometer.** In optical pyrometer the intensity of radiation of a certain wave length emitted by a hot body is compared with that of the radiation of the same wavelength emitted by a standard body. The instrument is adjusted until the two intensities are equal. The temperature of the hot body must then be equal to that of the standard body.

The pyrometer as shown in Fig. 12.14 consists of a telescope having an objective lens at one end and an eye piece E at the other end. An electric lamp having a straight filament F is placed in the

position of cross-wires with limiting diaphragms DD , on either side of it. The filament of the lamp can be heated to various temperatures by adjusting the strength of the current passing through the filament. The current in the battery circuit is measured with the help of a sensitive milliammeter A .

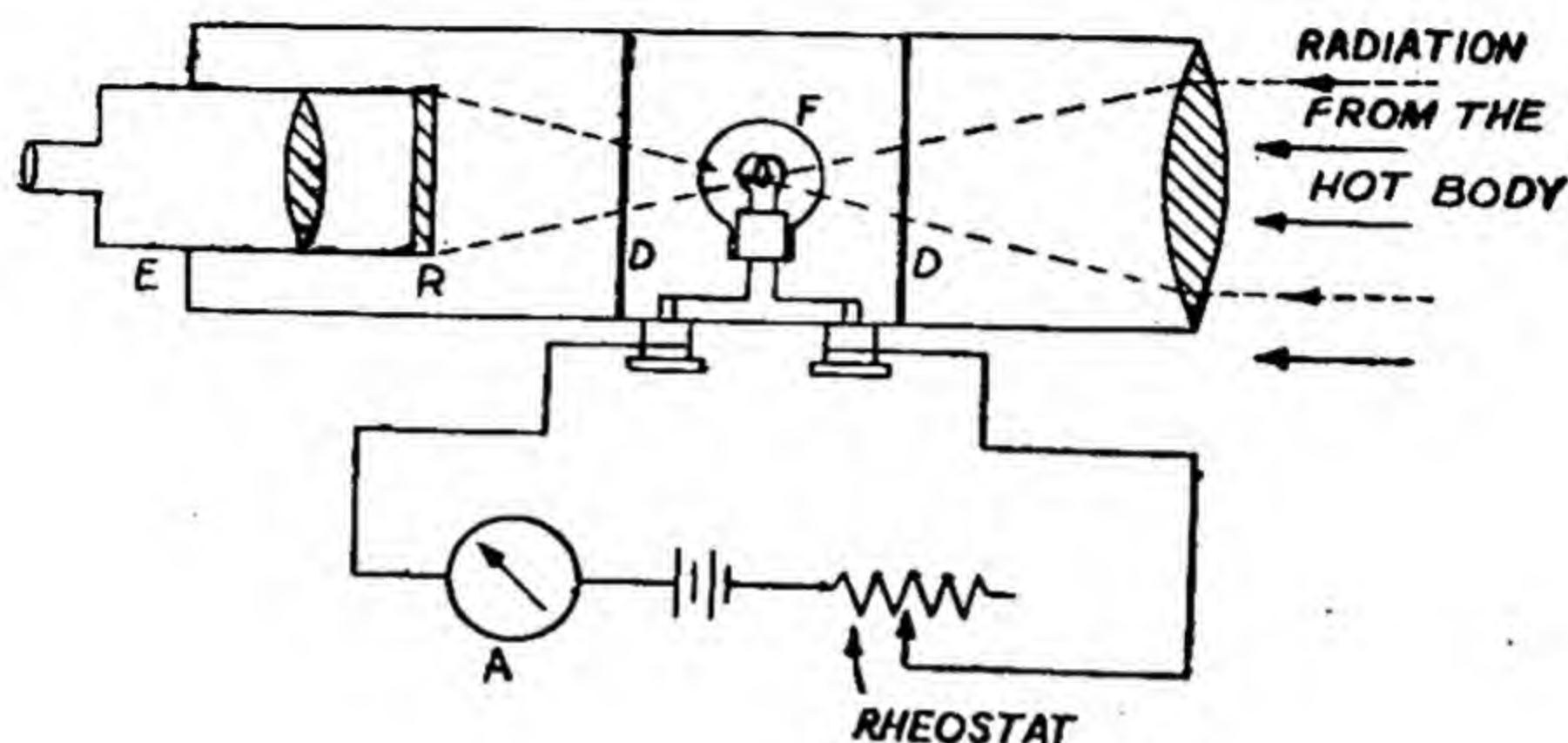


Fig. 12.14.

By adjusting the position of the objective, the radiations from the hot body are focussed on the filament of the lamp. Now the current is passed through the filament which is viewed through the eye piece. A thin plate of red glass R is placed at the position shown in Fig. 12.14 to restrict radiations from both sources within a narrow band of red wave lengths. In this way we look at the filament against the back ground of the hot body. If the current in the filament is too strong, then the filament will appear brighter than the image of the source. If the current is too weak it will appear dark as compared to the image. The current is so adjusted that the filament becomes invisible against the image of the source. When such is the case the temperature of the filament and that of the hot body is the same. In other words, the filament optically disappears hence the name **Disappearing Filament type optical pyrometer**. The red glass helps the eye to match the two images approximately for monochromatic radiation as it allows only a narrow band of wave lengths to pass through.

The temperature of the filament is calculated from the formula

$$I = a + bT + cT^2$$

where T is the absolute temperature, a , b and c are constants which can be determined by calibrating the instrument against three known temperatures such as the melting points of different metals.

For industrial work, the mill-ammeter may also be calibrated directly in degrees by focusing the instrument on a black body which can be maintained at various temperatures measured by sensitive thermo-couples.

The normal range of temperature which can be measured with this instrument is 600°C to 1500°C as beyond the maximum limit the filament rapidly deteriorates.

Modification for measurement of very high temperatures. For the measurement of temperatures higher than the normal range a rotating sector is employed to cut out a known fraction of the incident radiations. Suppose an opaque disc from which a sector θ is cut off as shown in Fig. 12.15 is rotated about the axis of pyrometer tube between the hot body and the objective of the telescope. If T_1 is the temperature measured by the instrument, then according to Stefan's Law, we have

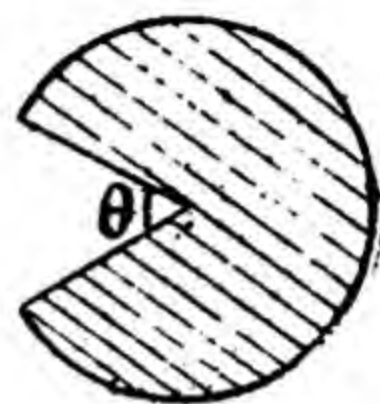


Fig. 12.15.

If T_2 is the actual temperature, then

$$T_1^4 \propto \theta$$

$$T_2^4 \propto 360$$

$$\therefore \frac{T_1^4}{T_2^4} = \frac{\theta}{360}$$

$$\therefore T_2 = T_1 \left(\frac{360}{\theta} \right)^{\frac{1}{4}}$$

Suppose $\theta = 22.5^{\circ}$ and the temperature T_1 indicated by the instrument is 1500°K , then

$$\begin{aligned} T_2 &= 1500 \left(\frac{360}{22.5} \right)^{\frac{1}{4}} \\ &= 1500 (16)^{\frac{1}{4}} \\ &= 1500 \times 2 = 3000^{\circ}\text{K} \end{aligned}$$

12.8. International Scale of temperature. We have seen above in several places that different types of thermometers have different scales of temperatures and no scale of temperature agrees with the other throughout its range except at the two fixed points. To overcome this disadvantage in accurate scientific measurements it was considered essential that some particular scale of temperature should be chosen as the standard. For achieving uniformity in the accurate statement of temperature for scientific work, the matter was studied by international committee of Weights and Measures who adopted in 1927, a practical scale of temperatures known as the *international temperature scale*. On this scale a series of freezing points and boiling points of substances in a given state of purity are obtained by the constant volume hydrogen thermometer. These fixed points, which are conveniently and accurately reproducible, together with specified means of interpolation, provide a practical scale of temperatures

which gives the closest possible realization of Thermodynamic scale and at the same time permits of uniformity of temperature statement.

The temperature were designated on this scale by “°C” or “°C (int)”. The introduction of this scale has facilitated the task of standardising thermometers by the standard laboratories all over the world.

The particulars of the instruments required and the formulae to be used to realize the temperatures between the fixed points have also been specified.

Basic fixed points.

(a) Boiling point of liquid oxygen	-182.970°C
(b) Melting point of ice	0.000°C
(c) Boiling point of water	100.00°C
(d) Boiling point of Sulphur	444.6°C
(e) Melting point of Silver	960.8°C
(f) Melting point of Gold	1063.0°C

The scale is divided into four parts for the purpose of interpolation. The methods of interpolation are briefly given as under.

(i) **From 0°C to 660°C .** Measurements are made by platinum resistance thermometer by using the formula

$$R_t = R_0 (1 + \alpha t + \beta t^2)$$

The constants R_0 , α and β are to be determined by measuring the resistance of the thermometer at the ice, steam and sulphur points respectively.

(ii) **From -190°C to 0°C .** The temperature is deduced from the resistance R_t of a standard platinum resistance thermometer in (i) above by means of the formula.

$$R_t = R_0 [1 + \alpha t + \beta t^2 + \gamma (t - 100) t^3]$$

The constants R_0 , α , β and γ are determined by measurements of resistance of the thermometer at the ice, steam, sulphur and oxygen points.

(iii) **From 660°C to 1063°C .** A thermo-couple, one wire of which is made of platinum the other being of an alloy of 90% platinum and 10% Rhodium, is maintained with one junction at 0°C . The diameter of each wire must lie between 0.35 and 0.65 mm. Temperature is given by the formula

$$E = a + bt + ct^2$$

where a , b and c are determined by measurements at the antimony, silver and gold points while E is the e.m.f. developed.

(iv) **From 1063° upwards.** For temperatures higher than the gold point, an optical pyrometer method is used. The intensity E_s of

monochromatic visible radiations of any convenient wave length λ emitted by a black body at a temperature t is compared with the intensity E_1 of radiation of the same wave length emitted by the black body at the gold point. The temperature is determined by the following formula known as Planck's radiation law.

$$\log \frac{E_2}{E_1} = \frac{C_2}{\lambda} \left[\frac{1}{1336} - \frac{1}{(t+273)} \right]$$

where C_2 is a constant taken as 1.432 cm-degrees.

Expected Questions

1. What are the lower and upper fixed points generally used? What numbers are given to these points on centigrade scale and Fahrenheit scales?
 2. Describe platinum resistance thermometer. How would you calibrate a thermometer of this kind and how would you use it to determine a given temperature on the gas thermometer scale?
 3. What are Pyrometers? What is the basis of Fery's Total Radiation Pyrometer? Which factor sets an upper limit to its maximum temperature measurement? Suggest a method for extending its temperature range.
 4. Give the theory of an optical pyrometer. What is its range of temperature? Can it be extended? How?
 5. (a) Explain the following. :—
 - (i) International scale of temperature.
 - (ii) Choice of metals in thermo-electric thermometer.
 - (b) What types of instruments would you use for the accurate measurement of temperatures in
 - (i) a boiler furnace
 - (ii) a steam pipe carrying highly super heated steam.
-

THERMODYNAMICS

13.1. Thermodynamics. It deals with the behaviour of gases and vapours under variations of temperature and pressure, and any process that produces a change in the properties is known as *Thermodynamic process*. For any process to be performed, a working substance is essential, which is termed as *thermodynamic medium*. In case of steam engines this working substance is water or steam, where as in case of internal combustion engines it is air.

[**Note.** The working substance is the agent which enables the heat engine to do its work. In principle, it does not matter what sort of fluid it is.]

13.2 First Law of Thermodynamics. This law may be stated in two slightly different forms.

(i) The first form of this law is one which establishes equivalence between mechanical work and the heat energy. To be more specific it can be stated as follows :

"When transformation of heat energy takes place into the mechanical energy (work), the amount of work performed is proportional to the amount of heat energy which disappears, and if the transformation occurs in the opposite direction, the heat energy produced is exactly equivalent to the mechanical energy consumed."

For example, for producing one calorie, of heat 4.2 joules of work must always be done some how. In general if W is the amount of work done and H is the corresponding amount of heat produced,

then

$$W = JH$$

where J is the mechanical equivalent of heat and has a value given by

	$J = 4.2 \text{ joules/cal.}$
or	$J = 4.2 \times 10^7 \text{ ergs/cal.}$
or	$J = 4200 \text{ joules/k. cal.}$
or	$J = 778 \text{ ft. lbs./B.H.U.}$
or	$J = 1400 \text{ ft. lbs./C.H.U.}$

(ii) It is a fundamental principle that energy can neither be created nor destroyed but only converted from one form to another. The sum total of energy in a closed system is found to remain always the same. This is known as principle of conservation of energy. Extending this general, law, it is stated that,

“In all transformations, the heat energy supplied to a substance is equal to the increase in internal energy of the substance plus external work done by the substance,

It can be symbolically stated as :

$$dQ = dE + dW$$

$$dQ = \text{heat transferred}$$

$$dE = \text{change in internal energy } (m C_v dT)$$

$$dW = \text{the external work done } (\int P dV)$$

13.3. Second Law of Thermodynamics. The first law only gives the equivalence between the quantity of heat used and the mechanical work done. But it does not give any idea of the extent to which the transformation of one type of energy into another can proceed. This is given by “Second Law of Thermodynamics” which has been enunciated by Clausius and Kelvin in slightly different words.

(a) (i) **Clausius’ statement.** “It is impossible for a self-acting machine working in a cyclical process, unaided by any external agency to convey heat from a body at a lower temperature to a body at a higher temperature.”

(ii) Heat cannot flow from a cold body to a hot body without the performance of work by some external agency.

(b) **Kelvin’s statement.** It is impossible to derive continuous supply of work by cooling a body to a temperature lower than that of the coldest of its surroundings.

The above statements give that no actual or ideal heat engine operating in cycles can convert into work all the heat energy supplied to the working substance. But whatever the conversion may be there, it will essentially be in the ratio of the mechanical equivalent of heat from the first law. This leads us to define the thermal efficiency.

Thermal Efficiency. It is the ratio of the heat converted into useful work to the heat supplied.

Thus thermal efficiency

$$\begin{aligned} \eta &= \frac{\text{Heat converted into useful work}}{\text{Heat supplied}} \\ &= \frac{\text{Heat supplied} - \text{Heat rejected}}{\text{Heat supplied}} \\ &= 1 - \frac{\text{Heat rejected}}{\text{Heat supplied}} \end{aligned}$$

Most efficient heat engines i.e., petrol and diesel engines do not have thermal efficiencies much above 40%. Steam turbine etc. has an efficiency of nearly 30 to 35% and steam engine 8 to 10%.

13.4. Reversible processes and irreversible process.

(a) ~~Reversible process.~~ A reversible process is that which can be retraced in the opposite direction so that the working substance passes through exactly the same conditions as it does in the direct process.

(b) A process in which this does not take place is called an irreversible process.

Examples. (i) *Reversible process.* 1. All isothermal and adiabatic changes are reversible when performed *slowly*. In such a case it is assumed that there is no friction to be overcome as work done in overcoming friction is wasted. The process carried out is very slow, hence no energy is wasted in producing oscillations and eddy currents and hence no heat is lost by conduction, convection and radiation.

Under these conditions if heat is supplied to a given mass of a gas at constant pressure, it expands and does some external work. If the same amount of work is done on the gas in compressing it, the same quantity of heat will be given out.

2. Ice melts when a certain amount of heat is absorbed by it. The water so formed can be converted into ice if the same amount of heat is removed from it.

3. If the resistance of a thermocouple is neglected, there will be no heat produced due to Joule heating effect. In such a case Peltier heating or cooling is reversible. At a junction where a cooling effect results due to Peltier effect when current flows in one direction an equal heating effect is produced when the current is reversed.

(ii) ~~Irreversible process.~~ 1. Work done against friction is irreversible. It is because in reversing the direction of motion again work has to be done against friction.

2. Joule Kelvin effect is irreversible because on reversing the flow of gas, a similar cooling or heating effect is not observed. Similarly diffusion, conduction and radiation are also irreversible.

3. Heat produced by the passage of current through a resistance wire is irreversible. It is because even when the current is reversed the same effect is observed.

For a reversible change to be possible the following conditions must be satisfied :—

(i) The substance undergoing a reversible change must at all stages be in thermodynamic equilibrium with its surroundings.

(ii) There should be no friction and no loss of heat by way of conduction, convection and radiation etc.

13.5. Meaning of Cycle. External work is performed by a heat engine as a result of a series of processes or operations through which the

working substance is made to pass. If these operations are arranged in such an order that the substance is regularly brought back to its initial state, then these operations constitute a **cycle**. When the series is complete, the cycle may be repeated any number of times.

If the operations of a cycle are plotted on a P — V diagram, they form a closed figure, each operation being represented by its own

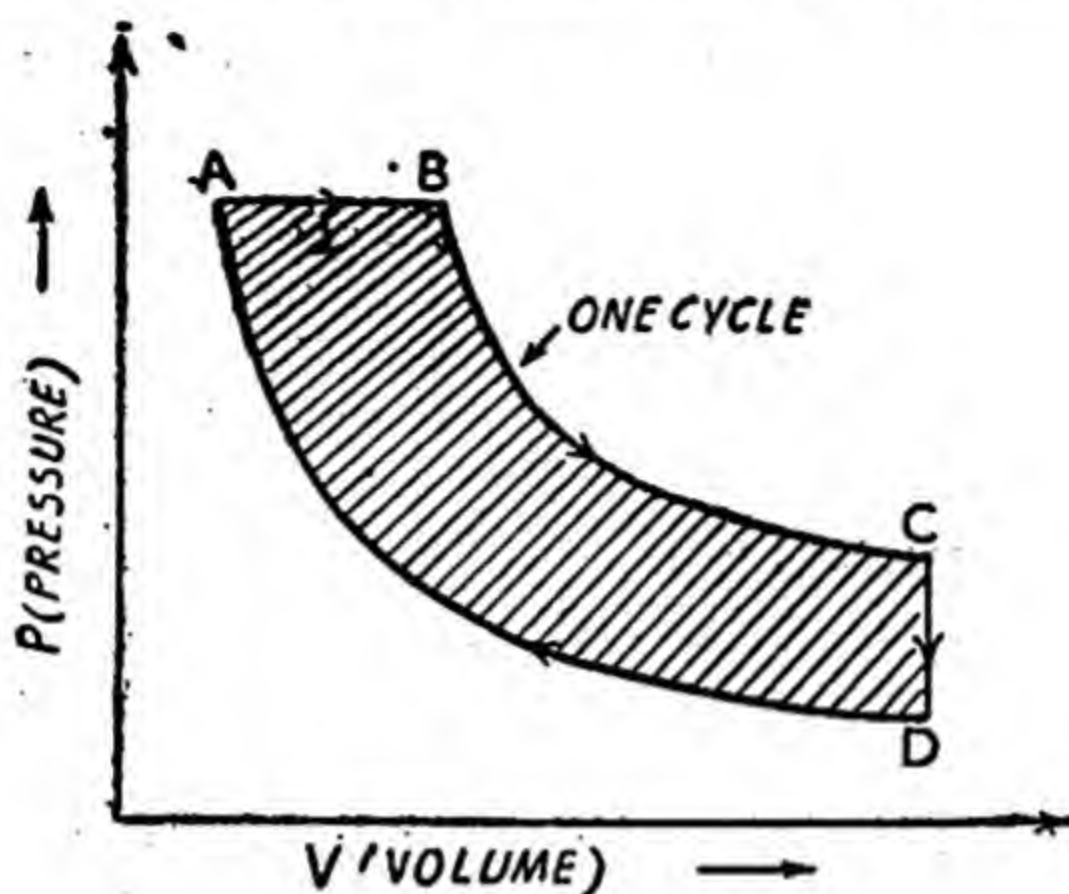


Fig. 13.1.

curve. The net amount of work done by the working substance during one complete cycle is given by the enclosed area of the P — V diagram shown shaded in Fig. 13.1.

The ideal cycle is one in which all the operations are reversible.

13.6. The Heat engine. The heat engine is a mechanical contrivance which enables a fluid, called the working substance, to go through a cycle of operations, as a result of which the mechanism can perform useful external work. As per *second law of thermodynamics* only a portion of the heat supplied to the engine is converted into useful work and the rest is rejected unused. The temperature at which heat is supplied to the working substance is always higher than that at which it is rejected. The hot body or *source* which supplies heat to the heat engine is called the *Heat source*, and the cold body into which unused heat is rejected is called the *Sink*. It is not possible to drive work from heat without a source and sink at different temperatures, at least no one has so far succeeded to do so. Also conversion of heat into work always involves a drop in temperature of the working substance. Depending upon the working substance used, the heat engines using water or steam are called steam engines (used in locomotives) and steam turbines (used in large electric power stations and in big ships). Those using working substance as air are known as internal combustion engines used in motor cars, aeroplanes etc.

Thus there are three essential parts of a heat engine. (i) Heat

Source (ii) Working substance (iii) Sink. In case of steam engines etc. these are the *Furnace, steam* and the *condenser*, and for internal combustion engines heat is produced by *igniting a mixture of air and petrol vapour*, the working substance as already stated is *air* and the sink is the *atmosphere*.

The actual heat engine is, of course, a very complicated machine, although it can be a very compact unit such as the engine of a motor car. Those engines which require two complete revolutions of the crank are known as 4-stroke engines, where as some require one complete revolution of the crank for their completion are known as 2-stroke engines.

The ideal heat engine is regarded as a frictionless machine, so that the consideration of mechanical losses due to friction does not arise when these operations are studied, but only the transformation of heat into work and work into heat. A French engineer, **Sadi Carnot** in the early part of the 19th century proved that *even with an ideal engine it was not possible to convert more than a certain percentage of heat into work, as a consequence of a law of Nature*. He also showed how the operations of a heat engine should be carried out in order that the efficiency might be maximum. We shall now see how he was able to establish these points.

13.7. Carnot's cycle and Carnot's engine. An ideal heat engine, free from all imperfections of actual engines and hence never realised in practice, was considered by Carnot for theoretical investigation as follows. The ideal engine consists of :

(i) A cylinder having *perfectly, non conducting walls and perfectly conducting bottom*. In it moves a perfectly non-conducting piston in a horizontal direction without friction. The cylinder contains air (which is supposed to behave like a perfect gas) as the working substance and is placed on a perfectly insulated stand.

(ii) A hot body to serve as a *source of heat* at a constant temperature T_1° absolute.

(iii) A cold body to serve as *sink* at a constant lower temperature T_2° absolute.

The source and sink are large reservoirs of heat so that their temperatures remain practically unchanged during any transfer of heat to or from the cylinder.

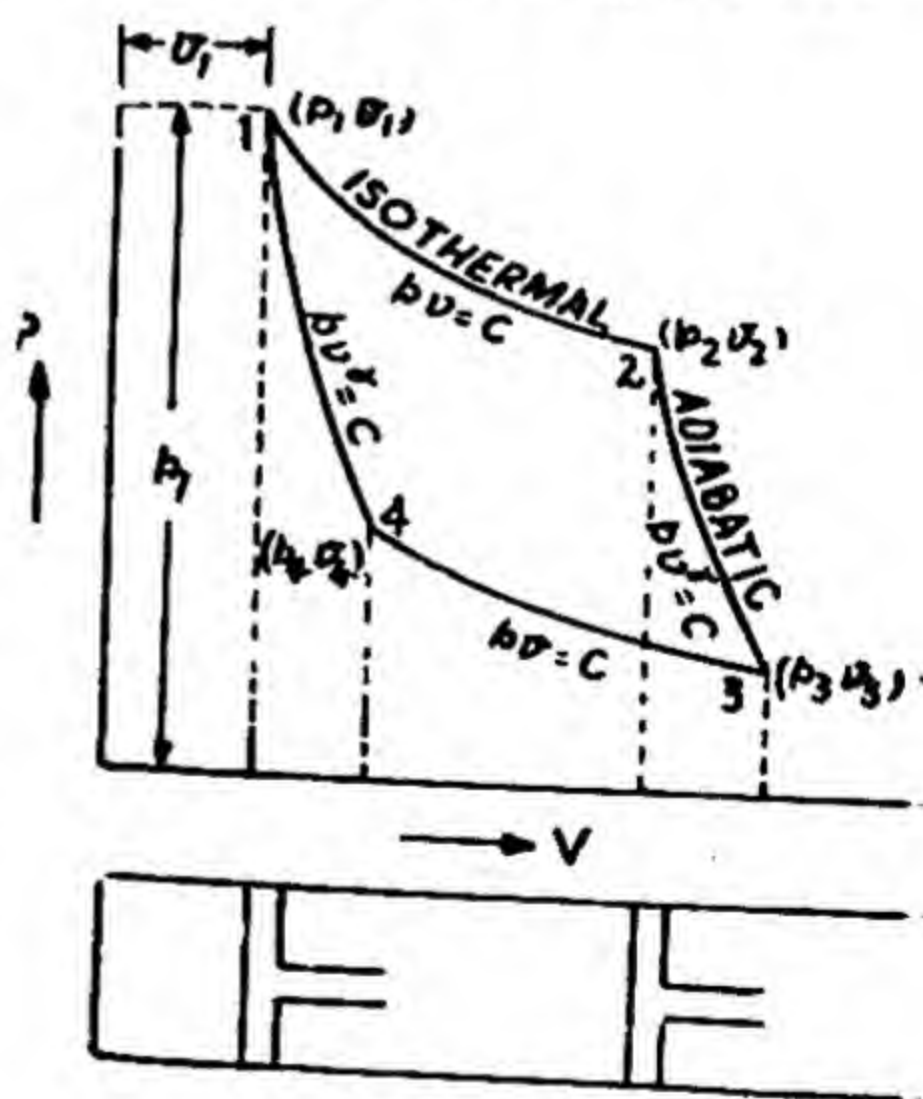


Fig. 13.2

Let the cylinder contain m gm. of air and let its original condition be represented by point (1) on the P — V diagram as shown in Fig. 13.2. In a Carnot's cycle the working substance is supposed to undergo the following four operations :—

(a) **Operation 1—2.** Let the initial temperature of the gas the cylinder be $T_1^\circ A$. Place it in contact with the source and let the piston move outward very slowly. As the piston moves, the gas expands and the temperature tends to fall. Heat is, therefore absorbed from the source at a constant temperature T_1 . The change is *isothermal* and is represented by the curve 1—2 in Fig. 13.2. The amount of heat absorbed Q_1 from the source is equal to the work done W_1 by the gas in free expansion from a pressure p_1 and volume v_1 at (1) to pressure p_2 and volume v_2 at (2).

$$\therefore W_1 = \text{Work done by the gas or air}$$

$$= mRT_1 \log_e \frac{v_2}{v_1} \text{ (already proved)}$$

$$\therefore Q_1 = \frac{mRT_1 \log_e \frac{V_2}{V_1}}{J}$$

$$\text{or } Q_1 = mART_1 \log_e \frac{V_2}{V_1}$$

(b) **Operation 2—3.** Now remove the cylinder from the source and place it on the perfectly insulated stand and allow the gas to expand adiabatically till its temperature falls to $T_2^\circ A$. The change is represented by adiabatic (2—3). The work done W_2 by the gas is given by the relation

$$W_1 = \frac{p_2 v_2 - p_3 v_3}{\gamma - 1} = \frac{mR(T_1 - T_2)}{(\gamma - 1)} \text{ (as already proved)}$$

(c) **Operation 3—4.** In order to bring the working gas back to its original pressure and volume remove the cylinder from the insulated stand and place it on the sink at a temperature $T_2^\circ A$. Move the piston very slowly inwards so that the gas is compressed and the temperature tends to rise. Heat is, therefore given to the sink at a constant temperature $T_2^\circ A$. The change is isothermal and is represented by the curve (3—4). The amount of heat Q_2 given to the sink is equal to the work done W_3 on the gas in compressing it from the volume v_3 at a pressure p_3 at 3 to the volume v_4 at a pressure p_4 at 4.

$$\therefore W_3 = -mRT_2 \log_e \frac{v_4}{v_3}$$

$$= -mRT_2 \log_e \frac{v_3}{v_4}$$

$$\therefore Q_2 = -mART_2 \log_e \frac{v_3}{v_4}$$

Operation 4—1. Remove the cylinder from the sink and again place it on the insulated stand. Allow the piston to move inwards so that the gas is compressed adiabatically until the temperature rises from T_2 to T_1 and the gas attains its original pressure and volume. The change is represented by the adiabatic 4—1.

Work done on the gas during the compression is

$$W_4 = -\frac{p_4 v_4 - p_1 v_1}{\gamma - 1} \quad \text{or} \quad -\frac{mR(T_2 - T_1)}{(\gamma - 1)}$$

$$= \frac{p_1 v_1 - p_4 v_4}{\gamma - 1} \quad \text{or} \quad \frac{R(T_1 - T_2)}{(\gamma - 1)}$$

13.8. Efficiency of Carnot's Cycle. It will be noticed that the work done by gas during adiabatic expansion (2—3) is equal to the work done on the gas during the adiabatic compression (4—1) i.e.

$$W_2 = W_4$$

Hence net work done $= W_1 + W_2 - W_3 - W_4 = W_1 - W_3$

Heat in put to gas is $Q_1 = mART_1 \log_e \frac{v_2}{v_1}$

Heat rejected by gas is $Q_2 = mART_2 \log_e \frac{v_3}{v_4}$

The net amount of heat absorbed in units of work $= Q_1 - Q_2$.

\therefore Net work done by gas is equivalent of $Q_1 - Q_2$

Hence Efficiency $= \frac{\text{Out put}}{\text{In put}}$

$$\text{or} \quad \eta = \frac{\text{Amount of heat converted into work}}{\text{Total amount of heat absorbed}}$$

$$= \frac{Q_1 - Q_2}{Q_1}$$

Since the points 2 and 3 lie on the same adiabatic

$$\therefore p_2 v_2^\gamma = p_3 v_3^\gamma$$

Similarly points 1 and 4 lie on the same adiabatic

$$\therefore p_4 v_4^\gamma = p_1 v_1^\gamma$$

The points 1 and 2 lie on the same isothermal at T_1°

$$\therefore p_1 v_1 = p_2 v_2$$

Similarly the points 3 and 4 lie on the same isothermal at T_2° .

$$p_3 v_3 = p_4 v_4$$

Multiplying corresponding sides of the above expression we get

$$v_1 v_2^\gamma v_3 v_4^\gamma = v_1^\gamma v_2 v_3^\gamma v_4$$

$$\text{or } v_2^{\gamma-1} v_4^{\gamma-1} = v_1^{\gamma-1} v_3^{\gamma-1}$$

$$\text{or } \frac{v_2}{v_1} = \frac{v_3}{v_4}$$

$$\text{Let } \frac{v_2}{v_1} = \frac{v_3}{v_4} = r$$

(r is isothermal expansion or compression ratio)

$$\therefore Q_1 = m A R T_1 \log_e \frac{v_2}{v_1} = m A R T_1 \log_e r$$

$$Q_2 = m A R T_2 \log_e \frac{v_3}{v_4} = m A R T_2 \log_e r$$

$$Q_1 - Q_2 = m A R (T_1 - T_2) \log_e r$$

$$\text{Now } \eta = \frac{Q_1 - Q_2}{Q_1} = \frac{m A R (T_1 - T_2) \log_e r}{m A R T_1 \log_e r}$$

$$\therefore \eta = \frac{T_1 - T_2}{T_1}$$

$$\text{or } \eta = 1 - \frac{T_2}{T_1}$$

which shows (i) that the efficiency depends only upon the temperature of the hot and cold bodies and is independent of the nature of the working substance.

If for a carnot's engine

$$T_1 = 273 + 100 = 373^\circ K$$

and

$$T_2 = 273 + 0 = 273^\circ K$$

then,

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{373 - 273}{373} = \frac{100}{373}$$

$$\% \text{age } \eta = \frac{100}{373} \times 100 = 27\%$$

It shows that even in an ideal heat engine operating on an ideal cycle, the maximum efficiency obtainable is approximately 27% i.e. a fraction of the heat energy has been converted into work and rest i.e. 73% of the heat energy remains unavailable, which is in accordance with *Second Law of Thermodynamics*.

(ii) 100% efficiency can be achieved only when T_2 reaches absolute zero although it is impossible to achieve it in practice.

13.8. Internal Combustion Engines. (I.C. Engines). Like steam engine, an internal combustion engine is also a heat engine which converts

part of the heat energy of fuel into mechanical work. In this engine the combustion of the fuel takes place internally that is inside the engine cylinder itself. Consequently, very high temperatures are produced in the cylinder which, if not kept down to proper values will damage the metal of the cylinder and the valves. As the high temperatures are produced, the thermal efficiency of an internal combustion engine is very much improved to 35 to 40%. Also because of the absence of auxiliary units like a boiler and condenser etc. which are in a steam engine, the unit is a compact one. It is because of these considerations that internal combustion engines have become so popular in all spheres and are in extensive use in numerous fields like auto-mobiles, locomotives, generating sets, submarines, ships, aeroplanes, and in several industrial units. Internal combustion engine has largely replaced the steam engine and at present time the steam turbine alone, is comparable to the internal combustion engine in the amount of horse power produced.

As mentioned in the above lines that in case of internal combustion engines the fuel is burnt inside the engine cylinder and it is made to give up its heat to the working substance i.e. air. The fuel used may be petrol, gas or oil. These engines can be classified on any of the following bases :—

- (a) Spark ignition (S.I.) Engine.
- (b) Compression ignition (C.I.) Engine.

(a) **Spark ignition engines.** In these engines petrol, paraffin and gas are used as the fuel. The charge admitted to the engine cylinder is a homogeneous mixture of petrol and air which is delivered in correct proportions depending upon the load on the engine by a popular device known as *carburettor*. The mixture is compressed in the cylinder and is ignited by an electric spark from the spark plug. These engines work on what is called an **Otto Cycle**.

(b) **Compression ignition engines.** These engines use heavy oil which can not be easily vaporised. The oil is introduced into the cylinder in a very fine spray, mixed with air. It should be noted that the ignition is not being effected here by an external agency as in case of *Otto Cycle*. It is entirely due to the high temperatures produced by the high compression of the air. No electric spark is needed for ignition. These engines work on what is called a *Diesel Cycle*.

12.9. Carnot's Theorem.

Assuming the truth of the second law of thermodynamics it can be shown that *no heat engine is more efficient than a reversible engine when working between the same two limits of temperatures*. This is known as **Carnot's theorem**.

Suppose we have two heat engines *A* and *B* working between the same two limits of temperatures T_1 and T_2 , i.e., heat is absorbed

at a temperature T_1 from the source and is rejected to the sink at a temperature T_2 . Suppose A is more efficient than B , then in B we may suppose that the length of the stroke is so adjusted that the work performed in a complete cycle is equal to that performed by A under similar circumstances.

Let A be coupled with B , by a suitable machinery so that when it works directly, it drives B in the reverse direction as shown in Fig. 13.3. Then during each complete cycle A will absorb a quantity of heat Q_1 at a temperature T_1 and reject a quantity Q_2 at a temperature T_2 . On the other hand when B traverses a cycle in the reverse direction, it will absorb a quantity of heat Q_2' at a temperature T_2 and will reject a quantity Q_1' at a temperature T_1 . Thus the amount of heat energy converted into work by the engine A , in the first case

$$= Q_1 - Q_2$$

and amount of heat energy converted into work by the engine B , in the second case

$$= Q_1' - Q_2'$$

Since the works performed in both the cases are equal

$$\therefore Q_1 - Q_2 = Q_1' - Q_2'$$

Now by supposition the efficiency of A is greater than that of B

$$\therefore \frac{Q_1 - Q_2}{Q_1} > \frac{Q_1' - Q_2'}{Q_1'}$$

$$\text{or} \quad \frac{1}{Q_1} > \frac{1}{Q_1'}$$

$$\text{or} \quad Q_1' > Q_1$$

$$\text{Similarly} \quad Q_1 > Q_2'$$

This shows that the quantity of heat Q_1' which B rejects into the source is greater than the quantity of heat Q_1 which A absorbs from it and the quantity of heat Q_2' which B absorbs from the sink is greater than the quantity of heat Q_2 which A rejects to the sink.

Hence during one complete cycle a quantity of heat $Q_1' - Q_1 = Q_2' - Q_2$ will be transferred from the sink at a temperature T_2 to the source at a higher temperature T_1 . Since no external agency is supposed to aid during the whole process heat passes from a body at a lower temperature T_2 to a body at a higher temperature T_1 without the performance of work by an external agency. This is not in accordance with the second law of thermodynamics.

Hence the efficiency of A is equal to the efficiency of B . Thus we see that no engine can have an efficiency greater than that of a

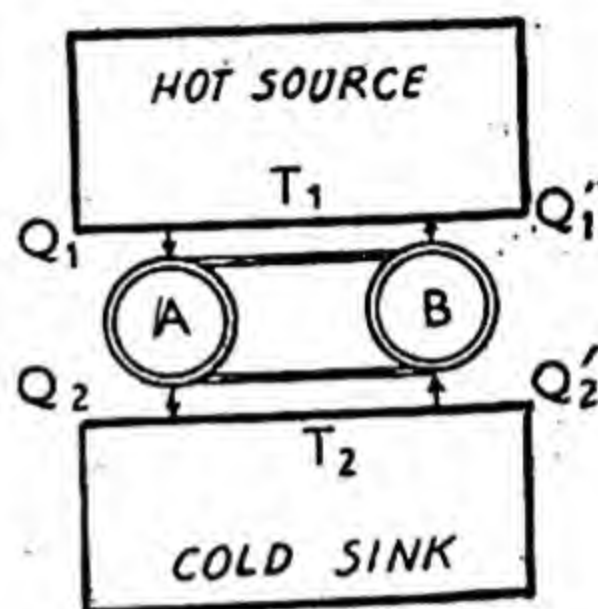


Fig. 13.3.

reversible engine.

Now the efficiency of a reversible heat engine is $\left(1 - \frac{T_2}{T_1}\right)$ when working between the temperatures T_1 and T_2 . This is independent of the nature of the working substance. Hence we see that the efficiency of all reversible heat engines working between the same limits of temperatures is the same, which is Carnot's theorem.

13.10. Clausius-Clapeyron's Equation. The boiling point as well as the freezing point of a liquid depends upon the pressure. It is possible to obtain a formula showing how the boiling point and freezing point changes with pressure by the application of the second law of thermodynamics. The relation thus obtained is known as Clausius Clapeyron's equation.

Consider a Carnot's engine having a unit mass of a liquid as the working substance in the cylinder. Let $aABb$ and $dDCc$ be the two isothermals for this substance at temperatures T° and $T^\circ - dT^\circ$ Absolute. Up to A the substance is wholly in a liquid state and along AB it exists partly in a liquid and partly in a vaporous state. The temperature T is, therefore, the boiling point of the liquid at a pressure corresponding to A . Similarly along the isothermal CD the liquid will be partly in a liquid and partly in a vaporous state at a temperature $T^\circ - dT^\circ$ Absolute. The temperature $T - dT$ represents the boiling point of the liquid at a pressure corresponding to D .

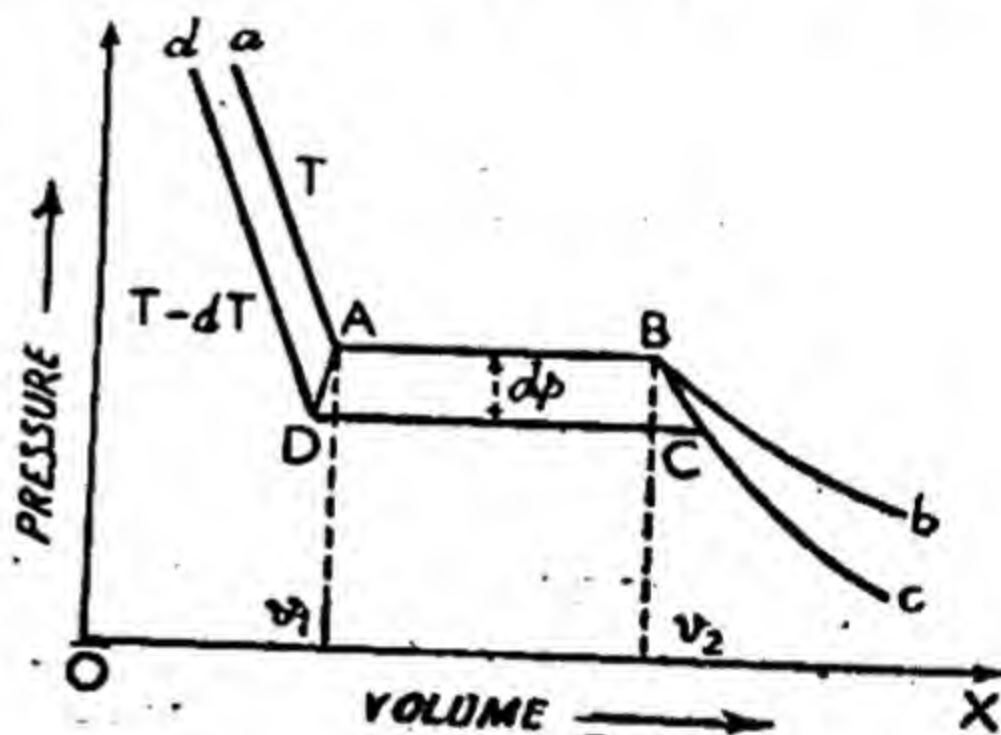


Fig. 3.4.

Let the volume of the liquid at A be v_1 c.c. Now

(i) Place the cylinder on the source at a temperature T . The liquid slowly gains heat and is converted into vaporous state at a constant pressure. The process is isothermal and is represented by AB . At B the whole of the liquid is converted into its vapour and occupies a volume v_2 c.c. If L is the latent heat of the liquid, then the amount of heat absorbed at $T^\circ = L$.

(ii) Place the cylinder on the non-conducting stand and allow the vapours to expand adiabatically so that the pressure decreases by a very small amount dp and the temperature falls to $T - dT$. This is represented by the adiabatic BC .

(iii) Again place the cylinder on the sink at a temperature $T - dT$ and compress the vapour very slowly so that the whole of the vapour is liquefied at a temperature $T - dT$, and the condition indicated by the point D is reached. The process is isothermal and a

quantity of heat $L-dL$ is given out at a temperature $T-dT$. Here $L-dL$ is the latent heat at this temperature.

(iv) Place the cylinder on a non-conducting stand and compress the liquid so that the initial volume and temperature as at A are attained. The process is adiabatic and is represented by the curve DA .

This is a reversible cycle because it can be performed in the opposite direction and each change in it can be reversed.

The efficiency of a reversible cycle is given by

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$\therefore \frac{L - (L - dL)}{L} = \frac{T - (T - dT)}{T}$$

or $\frac{dL}{L} = \frac{dT}{T} \quad \dots(i)$

The quantity of heat converted into work $= L - (L - dL) = dL$

Work done in one cycle $=$ area $ABCD$

$$= dp(v_2 - v_1) \text{ in work units}$$

$$= \frac{dp(v_2 - v_1)}{J} \text{ in heat units.}$$

\therefore If dL is measured in units of heat, then

$$dL = \frac{dp(v_2 - v_1)}{J} \quad \dots(ii)$$

Substituting the value of dL in equation (i), we have

$$\frac{dp(v_2 - v_1)}{JL} = \frac{dT}{T}$$

or $\frac{dp}{dT} = \frac{JL}{T(v_2 - v_1)} \quad \dots(iii)$

(1) **Effect of pressure on boiling point.** In equation (iii) if $v_2 > v_1$, i.e., there is an increase in volume when the liquid changes into its vaporous state, as is always the case, then $(v_2 - v_1)$ is positive. Since L is also positive.

$\therefore \frac{dp}{dT}$ is positive.

This shows that the boiling point of a liquid is raised by increase of pressure.

(2) **Effect of pressure on the melting point.** When a solid melts there may be an increase in volume as in the case of wax or there may be a decrease in volume as in the case of ice.

In the case of melting of wax $(v_2 - v_1)$ is positive, therefore, the melting point in this case is raised by increase of pressure as $\frac{dp}{dT}$ is positive.

In the case of melting of ice $(v_2 - v_1)$ is negative, hence the melting point is lowered by increase of pressure.

In general the melting point of those substances which expand on melting is raised by increase of pressure and vice versa.

13.11. Otto Cycle

The present day petrol (gasoline) engine operates on this Otto cycle because it was introduced in practical form by a German scientist Otto. This is also known as constant volume cycle.

The P - V diagram for a theoretical Otto cycle is shown in the Fig. 13.5.

The cycle consists of two constant volume lines and two adiabatic curves as shown. Let at a point 1, the cylinder be full of air of mass m gm. which has a volume of V_1 , pressure of P_1 and absolute temperature of T_1 . The cycle is completed in four stages described below.

(i) **First Stage.** The bottom of the cylinder is covered with the insulating cap and the piston is moved inwards compressing the air adiabatically till it reaches the end of its stroke at point 2. The pressure and temperature of the air rise to P_2 and T_2 respectively whereas its volume is reduced to a value of V_2 . Work is done on the air during this adiabatic compression.

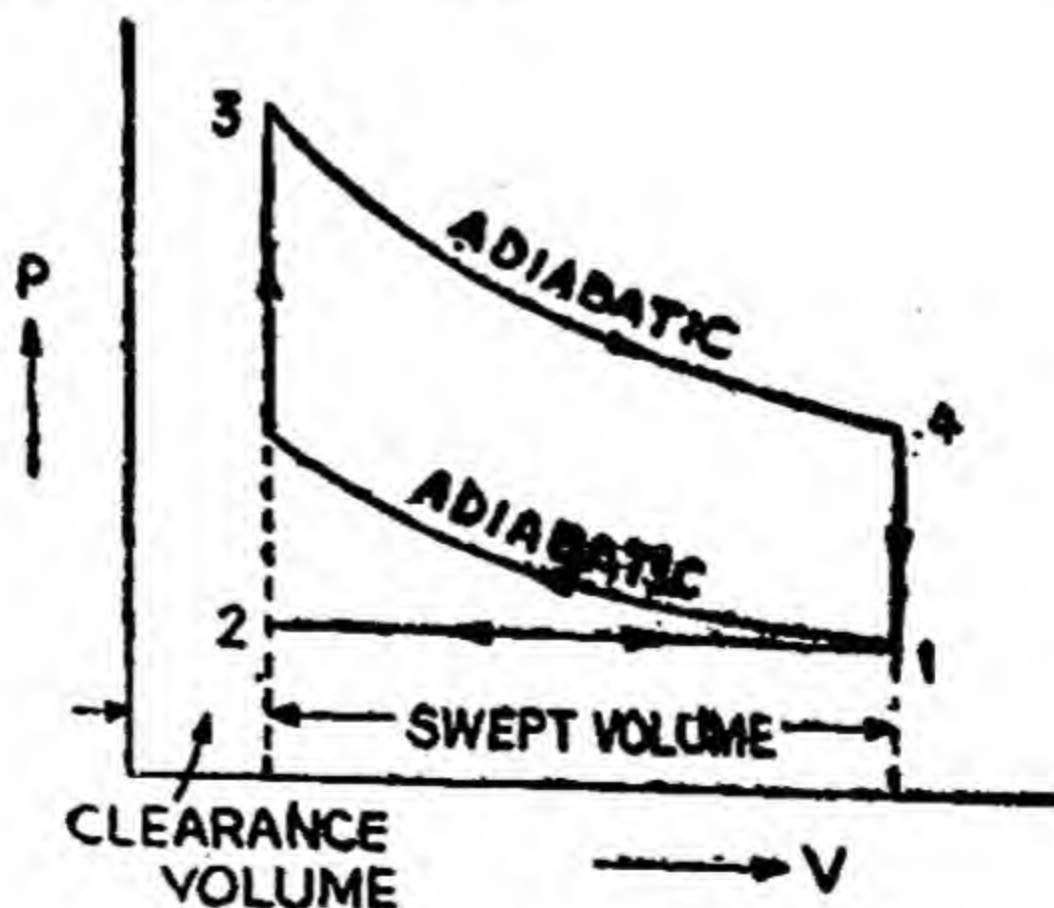


Fig. 13.5.

(ii) Second Stage

At point 2, insulating cap is removed, the cylinder bottom is brought in contact with the hot surface and then piston is held stationary. The air is heated at constant volume till its pressure and temperature rise to the values of P_3 and T_3 respectively. The heat taken in is

$$H_1 = mC_v(T_3 - T_2)$$

(iii) Third Stage

At point 3, hot body is removed and the insulating cap is again put on the bottom of the cylinder. The air is allowed to expand adiabatically till point 4 is reached. During this expansion, work is done by the air whose pressure and temperature fall to the values of P_4 and T_4 respectively.

(iv) Fourth Stage

At point 4, insulating cap is removed and the cylinder bottom is brought in contact with the cold sink. The piston is held stationary and the air is allowed to reject heat to the sink at constant volume till its pressure and temperature drop to their original values of P_1 and T_1 respectively. The amount of heat rejected to the sink is

$$H_2 = mC_v(T_4 - T_1)$$

The cycle is thus completed because the air has been brought back to the same conditions of pressure, volume and temperature as at the beginning of the cycle.

Ideal Efficiency

$$\text{Heat received } H_1 = mC_v(T_3 - T_2)$$

$$\text{Heat rejected } H_2 = mC_v(T_4 - T_1)$$

$$\text{Work done} = H_1 - H_2$$

$$\therefore \text{Efficiency} = \frac{H_1 - H_2}{H_1} = 1 - \frac{H_2}{H_1}$$

$$= 1 - \frac{mC_v(T_4 - T_1)}{mC_v(T_3 - T_2)}$$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Now from adiabatic compression AB , we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \dots (1)$$

Similarly from adiabatic expansion CD , we have.

$$T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}$$

or

$$\frac{T_4}{T_3} = \left(\frac{V_3}{V_4} \right)^{\gamma-1} \quad \dots(2)$$

Since $\frac{V_3}{V_4} = \frac{V_2}{V_1}$, hence from Equations (1) and (2) we get :

$$\frac{T_1}{T_2} = \frac{T_4}{T_3} \text{ or } \frac{T_3}{T_2} = \frac{T_4}{T_1}$$

or

$$\frac{T_3}{T_2} - 1 = \frac{T_4}{T_1} - 1$$

or

$$\frac{T_3 - T_2}{T_2} = \frac{T_4 - T_1}{T_1}$$

or

$$\frac{T_1}{T_2} = \frac{T_4 - T_1}{T_3 - T_2} \quad \dots(3)$$

Now

$$\eta = 1 - \frac{T_4 - T_1}{T_3 - T_2}$$

Substituting the value from Eq. (3) we have

$$\text{Air-standard Efficiency } \eta = 1 - \frac{T_1}{T_2}$$

Since $\frac{V_1}{V_2}$ = adiabatic compression ratio ρ

Hence

$$\frac{T_1}{T_2} = \left(\frac{1}{\rho} \right)^{\gamma-1}$$

\therefore Air-standard

$$\eta = 1 - \left(\frac{1}{\rho} \right)^{\gamma-1}$$

Actual P-V Diagram for Otto Cycle The theoretical P-V diagram of the Otto cycle shown in Fig 13.5 is some what modified when used in an internal combustion engine running on petrol or gas. The cycle involves six processes out of which four require movement of the piston and are called strokes. The engine is known as four-stroke engine. As shown in Fig. 13.6(i) the engine consists of a piston and a cylinder which is provided with inlet valves and exhaust valves. The six processes are as follows :—

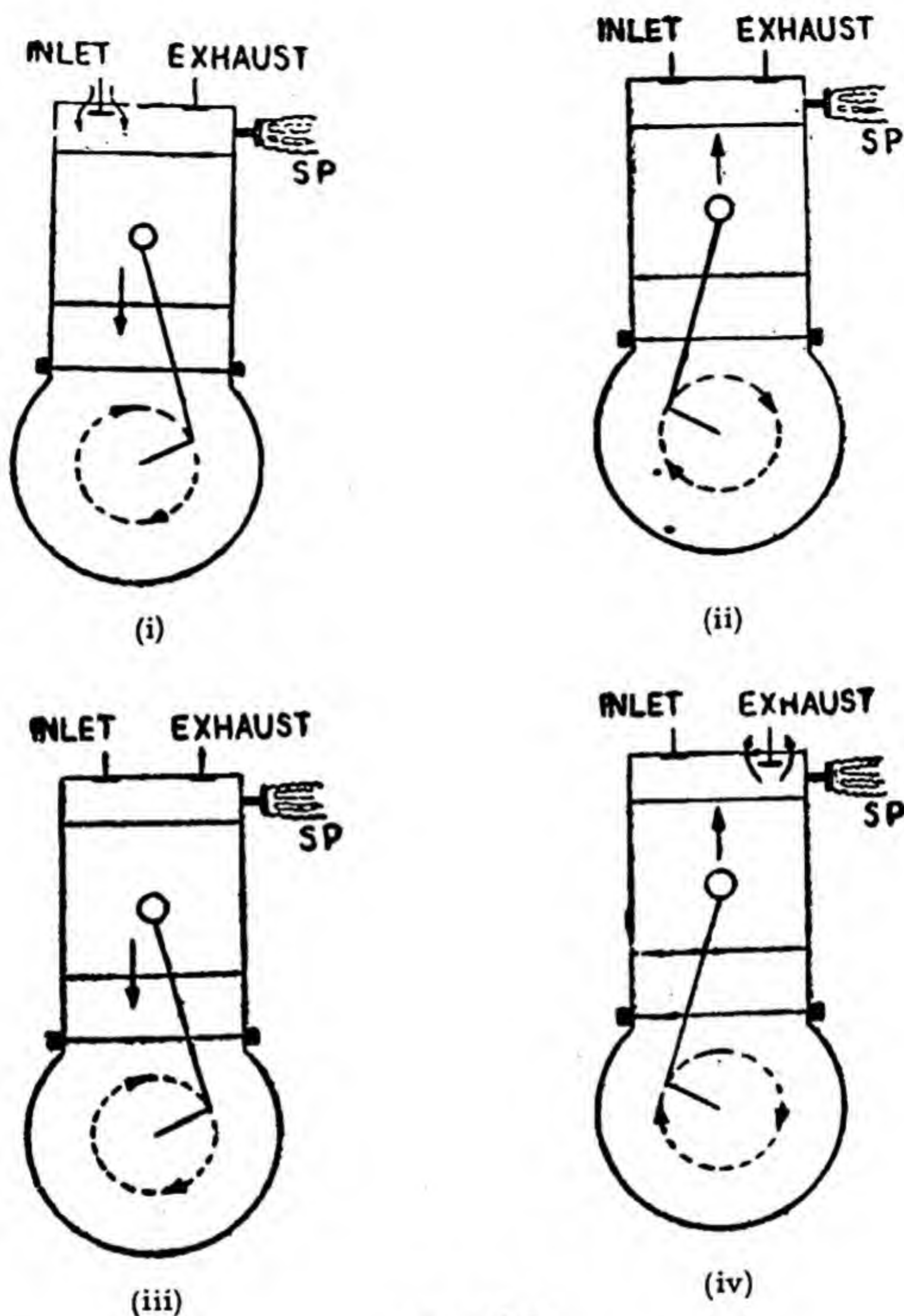


Fig. 13.6

(i) Suction or Charging Stroke

In this stroke, the inlet valve opens and a charge of explosive mixture of air and petrol vapours is drawn into the cylinder as the piston makes its first outstroke, at something like atmospheric pressure. This suction continues till piston reaches its bottom dead centre (BDC). This is shown by line 1,2 in the $P-V$ diagram.

(ii) Compression Stroke

In this stroke, all valves are closed and the explosive mixture is compressed adiabatically into the clearance space. The pressure and the temperature of the mixture increase considerably. The piston reaches its top dead center. This process is shown by the curve BC .

Explosion At or near the end of the compression stroke, the combustible mixture is fired by a series of electric sparks from outside. It burns with explosive violence thereby releasing heat energy. There

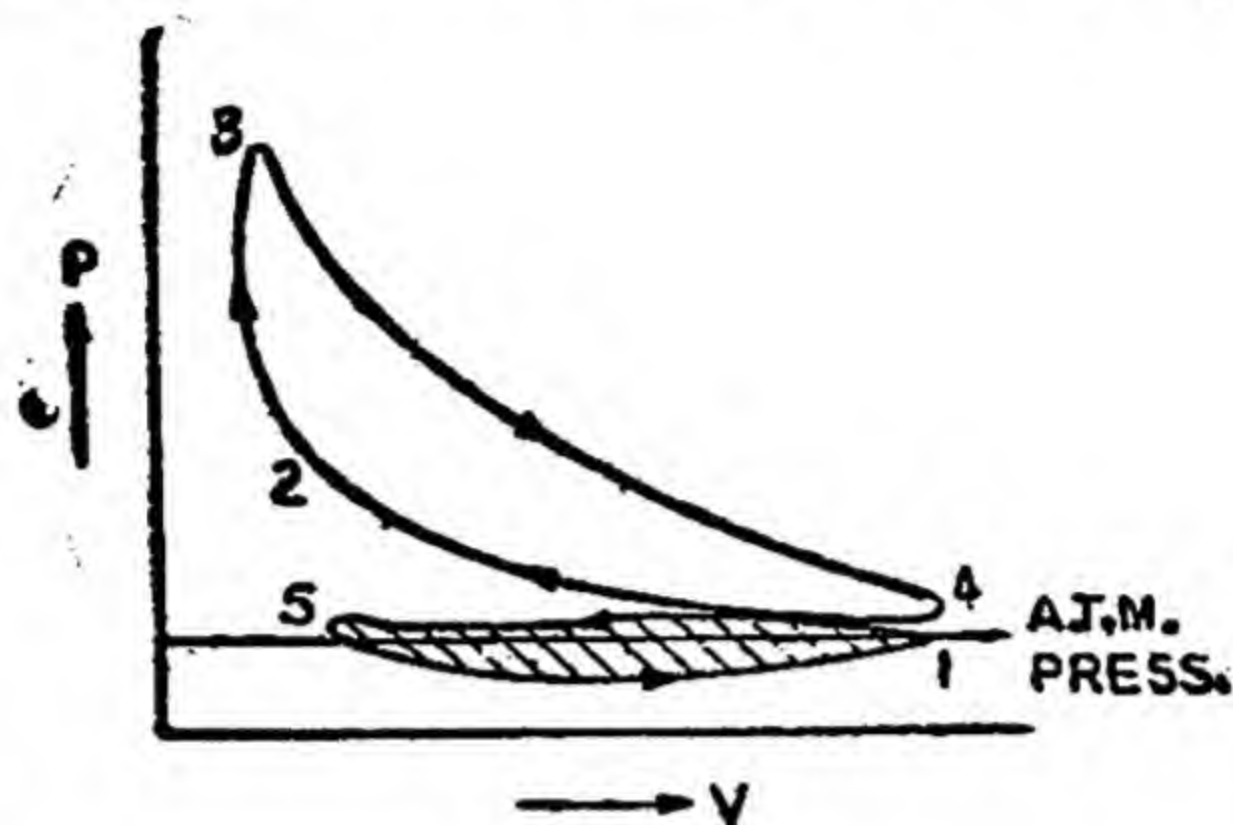


Fig. 13.7.

is a rapid rise in the pressure and temperature of the products of combustion but their volume remains practically constant. The piston does not move in this process. This combustion is shown by the curve CO which is practically a straight line.

(iii) Working or Power stroke

Due to the explosion of the mixture, the piston is pushed out with great force. The hot burnt gases expand, the expansion being approximately adiabatic due to the high speed of the piston. During the expansion DE some of the heat energy produced is transformed into work. The pressure and temperature of the burnt gases fall to the values represented by point E . Even though there is a good deal of energy in the hot gases, yet no further energy transformation can occur since the piston cannot go further (because it has already reached its BDC).

Exhaust. At the end of the power stroke i.e., at point E . The exhaust valve opens and allows gases to escape until the pressure drops to that of the atmosphere. Heat is rejected to the surroundings at practically constant volume (line EF).

(iv) Exhaust Stroke

FA represents the exhaust stroke during which the piston, while moving inwards, pushes the remaining burnt gases out. The cycle is completed and the cylinder is ready to draw in the next charge of air and petrol vapours or a mixture of air and gas. It is shown by line FA .

Example 1. A gas engine working on the Otto cycle has a cylinder of diameter 152.4 mm and a stroke of 221.6 mm. If the clearance volume

is 1310 cm^3 , find the air-standard efficiency of the engine, $\gamma = 1.4$.

$$\begin{aligned}\text{Swept volume} &= \frac{\pi}{4} D^2 \times \text{stroke length} \\ &= \frac{\pi \times (15.24)^2}{4} \times 22.86 = 4160 \text{ cm}^3.\end{aligned}$$

$$\begin{aligned}\text{Total volume} &= \text{Swept volume} + \text{clearance volume} \\ &= 4160 + 1310 = 5470 \text{ cm}^3\end{aligned}$$

$$\text{Compression ratio, } \rho = \frac{5470}{1310} = 4.18$$

$$\begin{aligned}\therefore \text{Air-standard } \eta &= 1 - \left(\frac{1}{\rho} \right)^{\gamma-1} \\ &= 1 - \left(\frac{1}{4.18} \right)^{1.4-1} \\ &= 0.43 \text{ or } 43\%.\end{aligned}$$

Example 2. The efficiency of an otto cycle is 50% and γ is 1.5. What is the compression ratio?

$$\text{Now } \eta = 1 - \left(\frac{1}{\rho} \right)^{\gamma-1}$$

Substituting the values :

$$50 = \left(1 - \frac{1}{\rho^{1.5-1}} \right) \times 100$$

$$\frac{50}{100} = 1 - \frac{1}{\rho^{0.5}}$$

$$\text{or } 0.5 = 1 - \frac{1}{\rho^{0.5}}$$

$$\text{or } \frac{1}{\rho^{0.5}} = 0.5 \quad \text{or } \rho = (2)^{\frac{1}{0.5}}$$

$$= (2)^2$$

$$= 4$$

\therefore Compression ratio = 4.

Example 3. Derive an expression for a change in efficiency for a change in compression ratio. If the compression ratio is increased from 6 to 8, what will be the percentage increase in efficiency?

Air standard efficiency

$$\eta = 1 - \frac{1}{\rho^\gamma - 1}$$

where

$$\gamma = 1.4$$

Let

ρ_1 = original compression ratio

ρ_2 = final compression ratio

$$\text{Original efficiency} = 1 - \frac{1}{\rho_1^{\gamma-1}}$$

$$\text{Final Efficiency} = 1 - \frac{1}{\rho_2^{\gamma-1}}$$

Percentage increase in efficiency

$$= \frac{\left(1 - \frac{1}{\rho_2^{\gamma-1}}\right) - \left(1 - \frac{1}{\rho_1^{\gamma-1}}\right)}{\left(1 - \frac{1}{\rho_1^{\gamma-1}}\right)} \times 100$$

$$= \left\{ \frac{\left(1 - \frac{1}{\rho_2^{\gamma-1}}\right)}{\left(1 - \frac{1}{\rho_1^{\gamma-1}}\right)} - 1 \right\} \times 100$$

Now

$$\rho_1 = 6$$

$$\rho_2 = 8$$

\therefore Percentage increase in efficiency

$$= \left\{ \frac{\left(1 - \frac{1}{(8)^{1.4-1}}\right)}{\left(1 - \frac{1}{(6)^{1.4-1}}\right)} - 1 \right\} \times 100$$

$$= \left\{ \frac{1 - \frac{1}{8^{0.4}}}{1 - \frac{1}{6^{0.4}}} - 1 \right\} \times 100$$

$$= 8\%$$

13.12. Theoretical Diesel Cycle

The Diesel Cycle, also known as the constant Pressure Cycle was first introduced by Dr. Rudolph Diesel. It consists of two adiabatics, one constant pressure line and one constant volume line. The engines used in heavy motor vehicles, stationery power plants, big industrial units and marine ships etc. use this cycle of operation.

The different stages of the cycle are shown on the PV diagram. To begin with let us suppose that the engine cylinder is full of air of mass ' m ' gms which has a pressure of P_1 , volume of V_1 and temperature of T_1 as represented by point 1.

First Stage

The piston moves inwards compressing the air adiabatically (according to the law $PV^r = \text{constant}$) upto point 2. The air now occupies the clearance space. The pressure, volume and temperature rise to P_2 , V_2 and T_2 respectively.

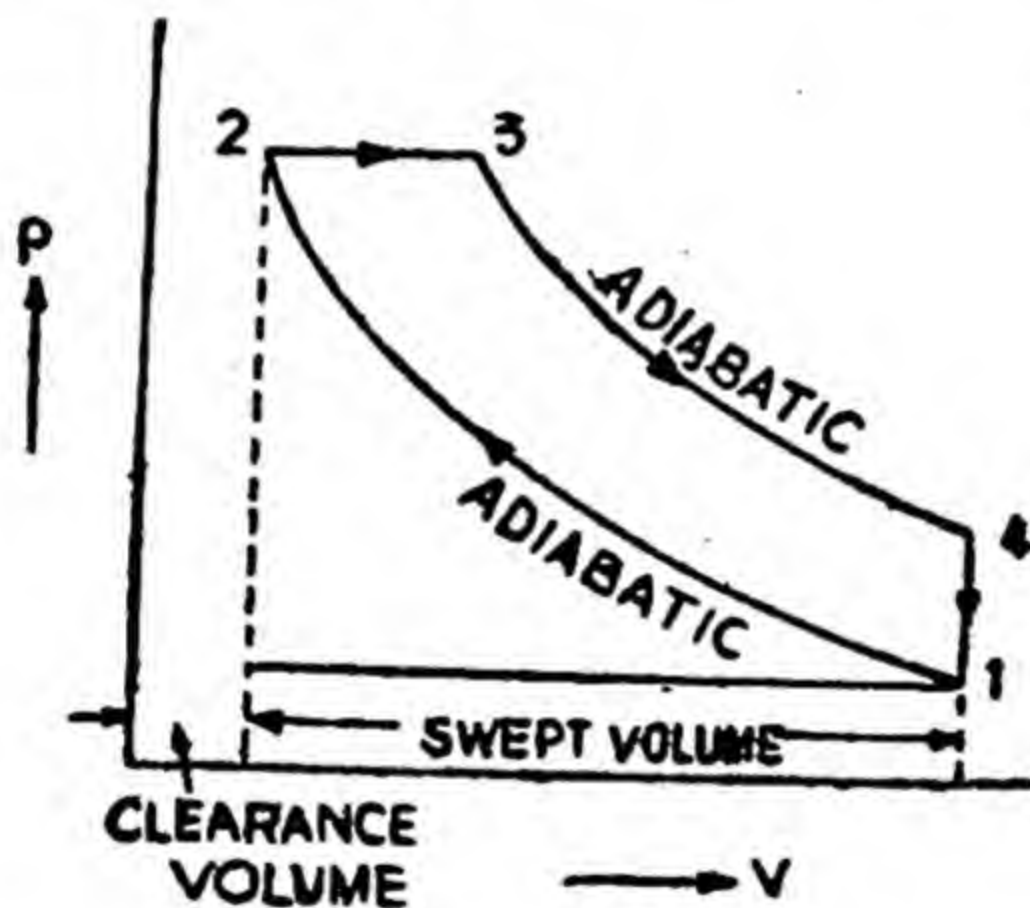


Fig. 13.8.

Second Stage

At point 2, heat is supplied to the compressed air from an external source of heat at constant pressure till point 3 is reached. The amount of heat absorbed is $Q_1 = m C_p (T_3 - T_2)$

Third Stage

At point 3, the heat supply is cut off and this point is known as the point of cut off. The air is allowed to expand adiabatically (according to the law $PV^r = \text{constant}$) till point 4 is reached.

Fourth Stage

At point 4, the hot air rejects heat to the sink at constant volume. The piston is held stationary during this process till the pressure falls to P_1 . This completes the cycle, since air is restored to its original conditions.

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The amount of heat rejected is given by

$$Q_2 = mC_v (T_4 - T_1).$$

13.13. Air-Standard Efficiency of Diesel Cycle

Heat received $Q_1 = m C_p (T_3 - T_2)$

Heat rejected out $Q_2 = mC_v (T_4 - T_1)$

Heat converted into work $= Q_1 - Q_2$

$$\therefore \text{Air standard efficiency} = \frac{Q_1 - Q_2}{Q_1}$$

$$= 1 - \frac{Q_2}{Q_1}$$

$$= 1 - \frac{mC_v (T_4 - T_1)}{mC_p (T_3 - T_2)}$$

$$= 1 - \frac{1}{\gamma} \frac{(T_4 - T_1)}{(T_3 - T_2)} \quad \because \left[\frac{C_p}{C_v} = \gamma \right]$$

$$\therefore \eta = 1 - \frac{1}{\gamma} \frac{(T_4 - T_1)}{(T_3 - T_2)}$$

Now Let $\frac{V_1}{V_2} = \text{adiabatic compression ratio} = r_1$

and $\frac{V_4}{V_3} = \text{adiabatic expansion ratio} = r_2$

and $\frac{V_3}{V_2} = \frac{V_3}{V_4} \times \frac{V_1}{V_2} = \frac{r_1}{r_2} = a \quad [\because V_1 = V_4]$

Then, $T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = T_1 (r_1)^{\gamma-1}$
 ...[Adiabatic compression]

Also $\frac{T_3}{T_2} = \frac{V_3}{V_2}$ or $T_3 = T_2 \cdot \frac{V_3}{V_2} = T_2 \cdot a$
 ...[constant Pressure Process]

$$= T_1 (r_1)^{\gamma-1} a$$

$$= a T_1 (r_1)^{\gamma-1}$$

Also $T_4 = T_3 \left(\frac{V_3}{V_4} \right)^{\gamma-1}$... (Adiabatic Expansion),

$$= T_3 \cdot \left(\frac{1}{r_2} \right)^{\gamma-1}$$

$$= a T_1 \left(\frac{r_1}{r_2} \right)^{\gamma-1}$$

$$= a \cdot T_1 (a)^{\gamma-1} = T_1 a^{\gamma}$$

Substituting the values of T_2 , T_3 , and T_4 , we have

$$\eta = 1 - \frac{1}{\gamma} \left[\frac{T_1 a^{\gamma} - T_1}{T_1 a r_1^{\gamma-1} - T_1 r_1^{\gamma-1}} \right]$$

$$= 1 - \frac{1}{\gamma} \left[\frac{a^{\gamma} - 1}{r_1^{\gamma-1} (a - 1)} \right]$$

Thus air-standard efficiency of a diesel is

$$\eta = 1 - \frac{1}{\gamma} \left[\frac{a^{\gamma} - 1}{r_1^{\gamma-1} (a - 1)} \right]$$

13.14. Steam Engine The reciprocating steam engine is one of the oldest types of heat engine which converts heat energy into mechanical work. It is an external combustion engine in which steam expands inside the engine cylinder doing work on the piston.

Although the steam engine is being largely replaced by the modern development of steam turbines and I. C. engines, it has still many specialised applications. A brief description of a simple steam engine is given below.

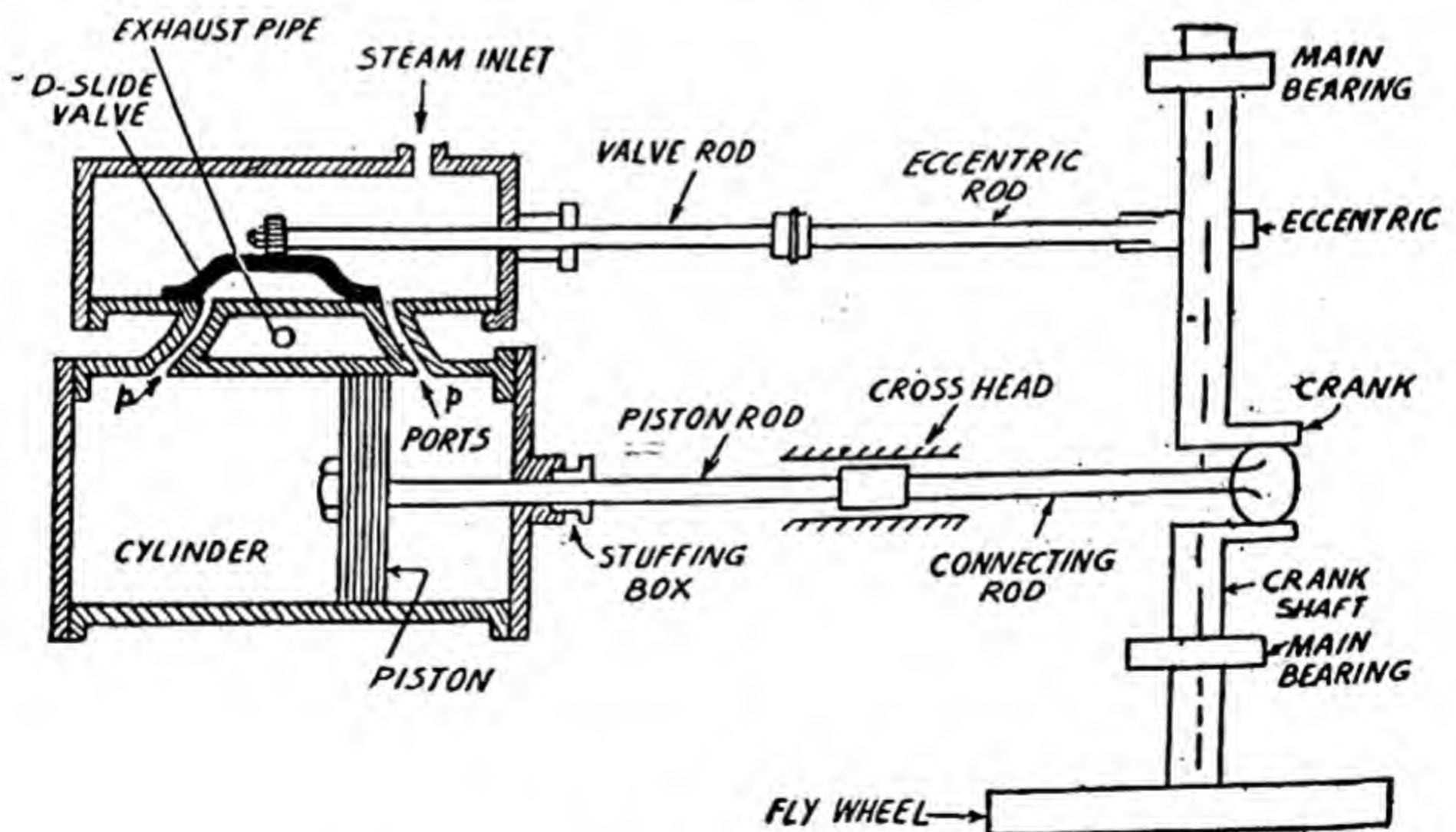


Fig. 13.9.

Reciprocating Steam Engine

The fig. 13.9. above shows outlines of a double acting reciprocating steam engine. There is a piston which reciprocates in the cylinder. There are two ports for admitting steam on either side of the piston inside the cylinder. Attached to the cylinder is the steam chest in which the D-side valve reciprocates and alternatively opens and closes the two

ports. The motion of this valve is taken from the crankshaft by means of an eccentric, eccentric rod and valve rod. Steam from the boiler plant is led to the steam chest. Steam enters into the cylinder and expands thus pushing the piston outwards. This thrust is transmitted to the crankshaft through the cross-head and connecting rod. When one stroke of piston is completed, the steam enters from the other side and pushes the piston inwards. Like this the piston reciprocates the reciprocating motion is converted into the rotory motion of the crankshaft.

13.15. Rankine Cycle

This is the standard cycle of operation which is employed for estimating and comparing the performance of various external combustion power plants. It is the ideal cycle on which a steam engine works. The P - V diagram is shown below :

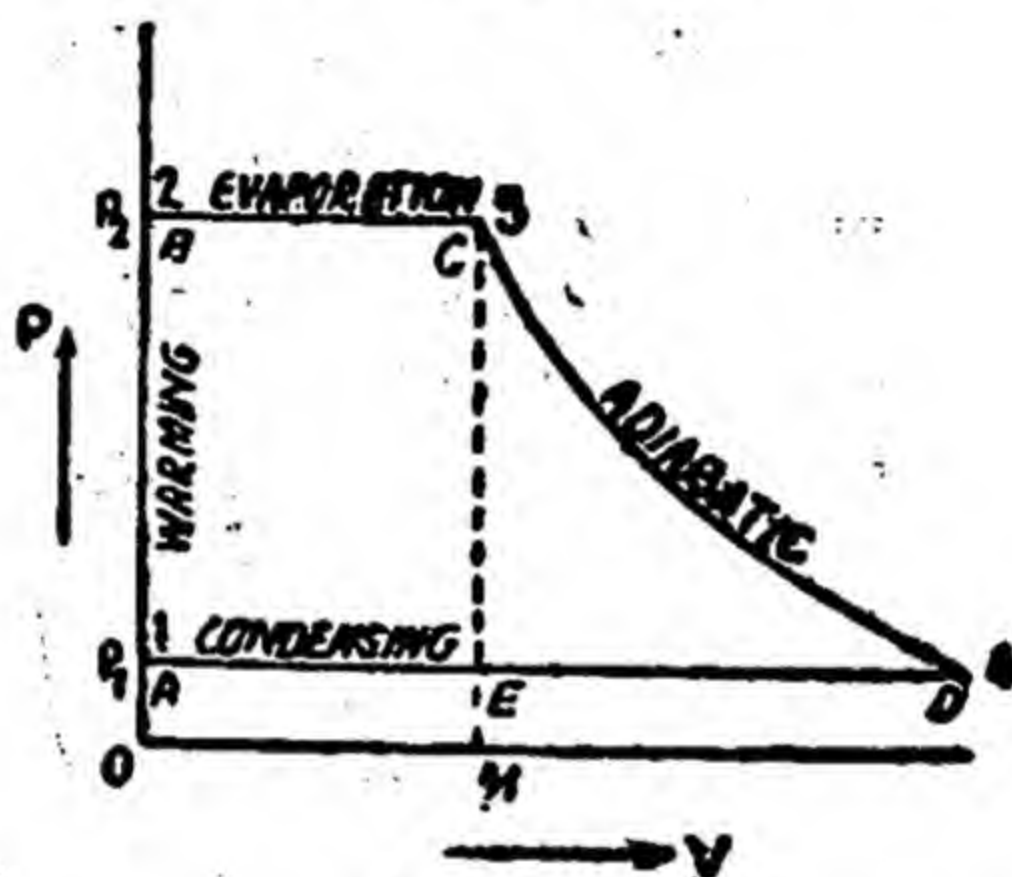


Fig. 13.10.

Consider 1 kg. of water at an initial temperature of T_2° absolute and under a pressure of P_2 kg/cm² absolute. This state of water is represented by the point A.

Operation AB. Let a hot body be brought in contact with this water in the cylinder, thus warming up water to an absolute temperature T_1 and a higher pressure P_1 .

Operation BC. Water is evaporated at constant pressure P_1 . Increase in volume takes place. Latent heat is absorbed by water and work is done due to increase in volume.

Operation CD. The hot body is removed and steam is allowed to expand adiabatically in the cylinder. The pressure of steam falls to P_2 and temperature to T_2 . Work is done on the piston by the expansion of steam.

Operation DA. A cold body is now brought in contact with the bottom of the cylinder and heat flows from steam to the cold body. Latent heat is rejected out by steam which condenses back into

water at constant pressure. Eventually, whole of steam gets converted into steam. Hence the cycle is completed.

The net work done by steam in one cycle is given by the enclosed area $ABCD$.

13.16. Efficiency of Rankine Cycle

Referring to the fig. 13.10. it can be seen that the heat is absorbed during the operations 'AB' and 'BC' while it is rejected during the operation 'DA'.

$$\begin{aligned}\text{Heat Input} &= \text{Heat absorbed during } AB + \text{heat absorbed during } BC \\ &= (Hw_1 - Hw_2) + q_1 L_1\end{aligned}$$

Where Hw_1 and Hw_2 are the enthalpies of water at B and A respectively, L_1 the latent heat of steam while q_1 is the dryness fraction of the steam

$$\begin{aligned}\text{Heat rejected} &= \text{Heat rejected during } DA \\ &= q_2 L_2 \\ \text{Work done} &= \text{Heat absorbed} - \text{Heat rejected} \\ &= (H_1 - Hw_2) - q_2 L_2 \\ &= H_1 - (Hw_2 + q_2 L_2) = H_1 - H_2 \\ \therefore \text{Efficiency} &= \frac{\text{Work done}}{\text{Heat Input}} = \frac{H_1 - H_2}{H_1 - Hw_2}\end{aligned}$$

$$\text{Thus Rankine Efficiency} = \frac{H_1 - H_2}{H_1 - Hw_2}$$

Note :—In actual practice, the cycle discussed above takes place in the steam engine plant as a whole. The water is pumped from the condenser at a pressure P_2 and temperatures T_2 into the boiler at the pressure P_1 and is heated to the temperature T_1 (operation AB). This water is then raised by the boiler into steam at pressure P_1 and dryness fraction q_1 (operation BC). The steam thus raised is then expanded adiabatically to the temperature T_2 and pressure P_2 (operation CD) in the engine cylinder. In the end the steam is exhausted and condensed in the condenser (operation DA) thus completing the cycle.

Example 4. Find the thermal efficiency of a Carnot's engine whose hot and cold bodies have temperatures of 2800°F and 60°F respectively. (A.M.I.E. 1958)

The thermal efficiency of a carnot engine

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$\begin{aligned}\text{Here } T_1 &= 2800 + 460 = 3260^\circ\text{K} \\ T_2 &= 60 + 460 = 520^\circ\text{K}.\end{aligned}$$

Substituting the values of T_1 and T_2 in the above relation we get,

$$\eta = \frac{3260 - 520}{3260} = 0.8407 \text{ or } 84.07\%$$

Example 5. A reversible engine converts one-sixth of the heat input into work. When the temperature of the sink is reduced by 62°C , its efficiency is doubled. Find the temperature of the source and the sink?

(A.M.I.E. 1959)

Since the engine converts $\frac{1}{6}$ th of the heat input into work

$$\begin{aligned} \therefore \eta &= \frac{1}{6} \\ \text{i.e. } \frac{T_1 - T_2}{T_1} &= \frac{1}{6} \end{aligned} \quad \dots(i)$$

Where T_1 is the temperature of the source and T_2 is the temperature of the sink.

When the temperature of the sink is reduced by 62°C , the efficiency is doubled i.e. it becomes $\frac{1}{3}$.

$$\therefore \frac{T_1 - (T_2 - 62)}{T_1} = \frac{1}{3} \quad \dots(ii)$$

$$\text{From (i), } 1 - \frac{T_2}{T_1} = \frac{1}{6}$$

$$\text{or } \frac{T_2}{T_1} = \frac{5}{6} \quad \dots(iii)$$

$$\text{from (ii), } 1 - \frac{T_2 - 62}{T_1} = \frac{1}{3}$$

$$\text{or } \frac{T_2 - 62}{T_1} = \frac{2}{3} \quad \dots(iv)$$

$$\text{from (iii), } T_2 = \frac{5}{6} T_1$$

Substituting this in (iv), we have

$$\frac{\frac{5}{6} T_1 - 62}{T_1} = \frac{2}{3}$$

Solving the above equations we have,

$$T_1 = 372^\circ\text{K or } 90^\circ\text{C}$$

$$\therefore T_2 = 310^\circ\text{K or } 37^\circ\text{C}$$

Example 6. In a diesel engine the compression ratio is 12 : 1 and the fuel is cut off at 8% of stroke. Calculate the air standard efficiency. (γ for air is 1.4.)

Let the clearance volume $V_2 = 1 \text{ m}^3$

then total cylinder volume $V_1 = 13 \text{ m}^3$
 and swept volume $(V_1 - V_2) = 13 - 1 = 12 \text{ m}^3$

8% of stroke volume $(V_3 - V_2) = \frac{8}{100} \times 12 = 0.96$.

Hence total volume to point of cut off $= V_3$
 $= \text{clearance volume} + 8\% \text{ of stroke}$
 $= 1 + 0.96 = 1.96$

$$\text{Air standard efficiency} = 1 - \frac{1}{\gamma} \cdot \frac{1}{r(\gamma-1)} \cdot \frac{a^\gamma - 1}{a - 1}$$

$$\text{or } \eta = 1 - \left(\frac{1}{r_1} \right)^{\gamma-1} \cdot \frac{(a^\gamma - 1)}{\gamma(a - 1)}$$

$$a = \frac{V_3}{V_2} = \frac{1.96}{1} = 1.96$$

$$r_1 = \frac{V_1}{V_2} = \frac{13}{1}$$

$$\therefore \eta = 1 - \left(\frac{1}{13} \right)^{1.4-1} \left[\frac{(1.96^{1.4} - 1)}{1.4(1.96 - 1)} \right]$$

$$= 0.583 \text{ or } 58.3\%$$

Expected Questions

- (a) Enunciate the first law of Thermodynamics.
 (b) State and explain the significance of the second law of thermodynamics.
 Give a brief summary of important implications of the second law.
- What is Carnot's theorem? How do you prove this theorem?
- Derive the clausius-clapeyron equation and show how with the help of it, one can determine the variation of boiling point and melting point with pressure variations.
- (a) What is Otto Cycle? Why it is known as four stroke engine?
 (b) Derive an expression for its efficiency.
- (a) Explain the four strokes of Diesel engine. Derive the expression for its efficiency.
 (b) Compare the constant volume and constant pressure cycles.

